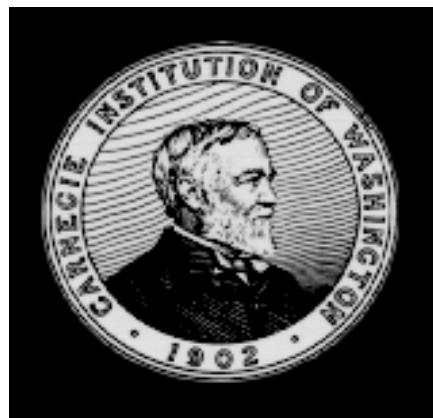


SYNCHROTRON RADIATION AND HIGH PRESSURE SCIENCE: Strongly Correlated Electron And Related Systems

Russell J. Hemley



*Geophysical Laboratory
Carnegie Institution of Washington,
Washington, DC*

*Carnegie/DOE Alliance Center
CDAC – NNSA
NSF COMPRES Consortium*

OUTLINE



- 1. Introduction**
- 2. Pressure-Tuning Oxides: FeO**
- 3. Novel Elemental Metals**
- 4. New Superconductors and Semiconductors**
- 5. Recent Technical Developments**

THEMES

- ***X-ray and IR***
- ***Integration of techniques***
- ***Diverse applications***

ADVANCES IN STATIC HIGH PRESSURE



PRESSURE UNITS

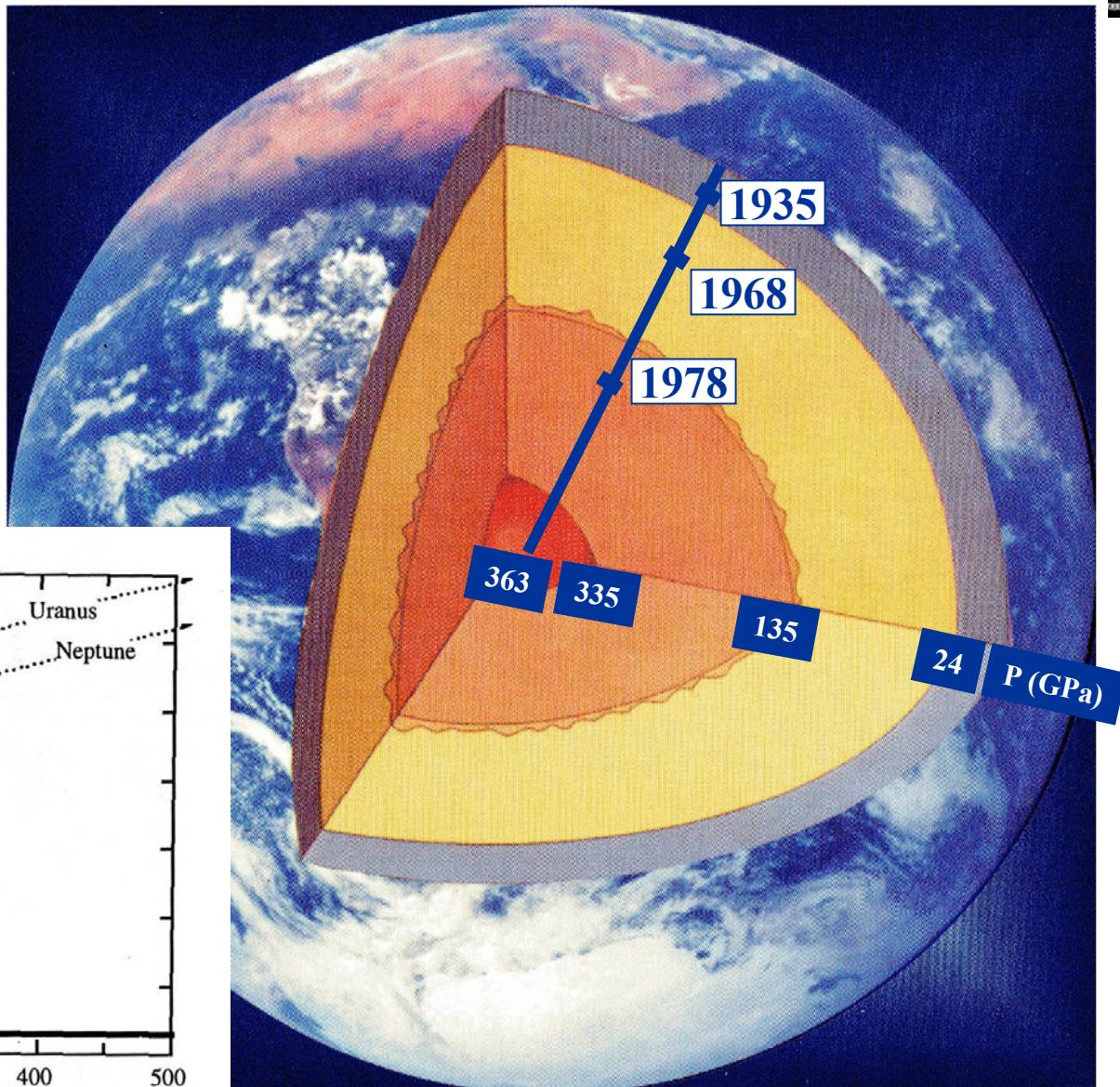
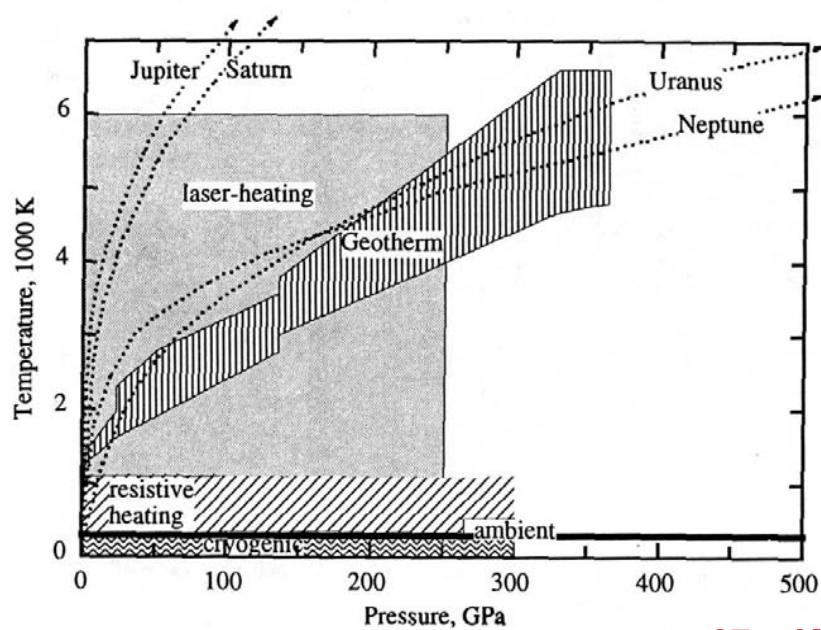
$10^3 \text{ atm} \approx \text{kbar}$

$10^6 \text{ atm} \approx \text{Mbar}$

$10 \text{ kbar} = 1 \text{ GPa}$

$1 \text{ Mbar} = 100 \text{ GPa}$

$1 \text{ Gigapascal} = 10^9 \text{ N/m}^2$



e.g., to 27 mK at 160 GPa

PRESSURE EFFECTS ON MATERIALS



- Pressure-tuning physical properties

- STRUCTURE
- ELECTRONIC BANDS
- VIBRATIONAL DYNAMICS
- MAGNETIC STATES
- QUANTUM FLUCUATIONS
- COUPLING OF DEGREES OF FREEDOM

- ‘Cleaner’ than chemical tuning
- New physical phenomena

e.g., 23 NEW ELEMENTAL SUPERCONDUCTORS UNDER PRESSURE

- New phases and novel materials

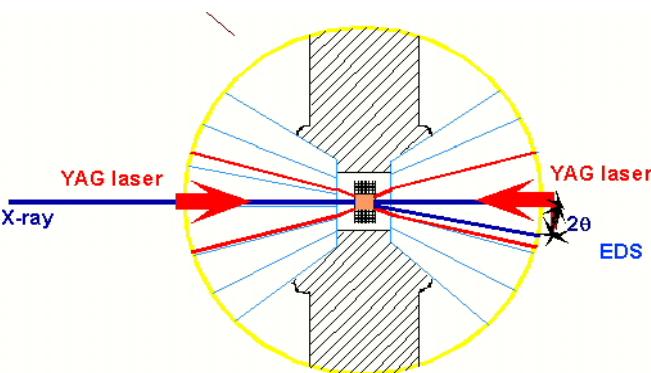
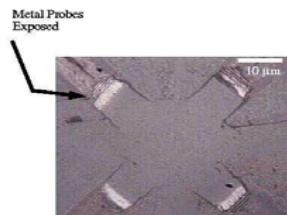
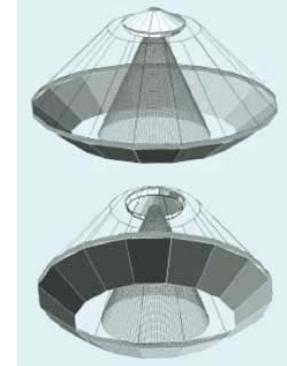
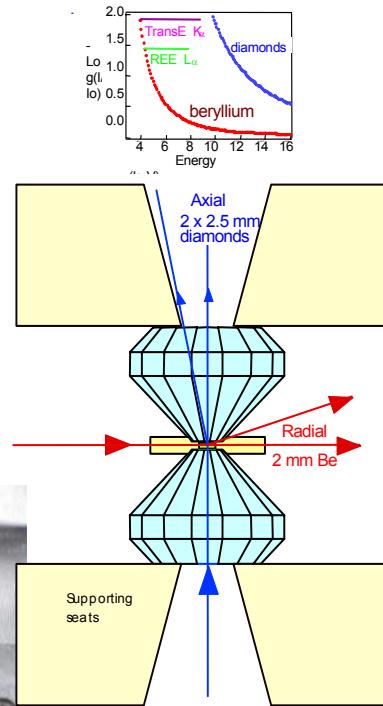
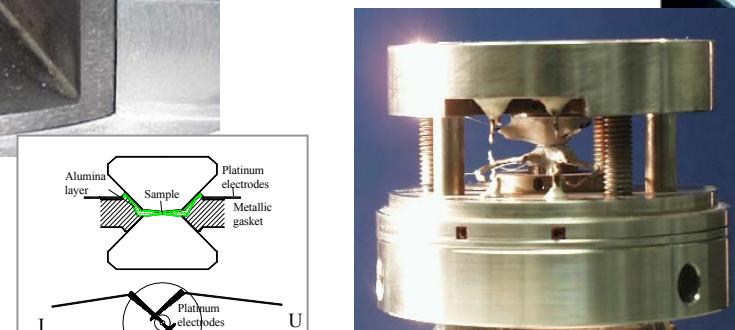
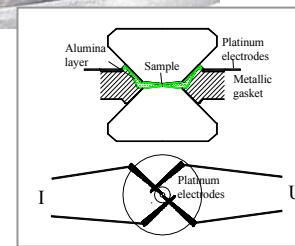
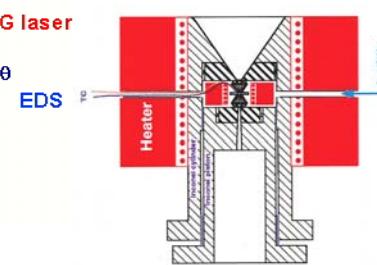
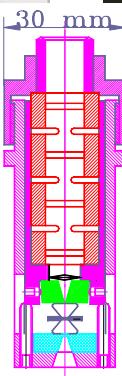
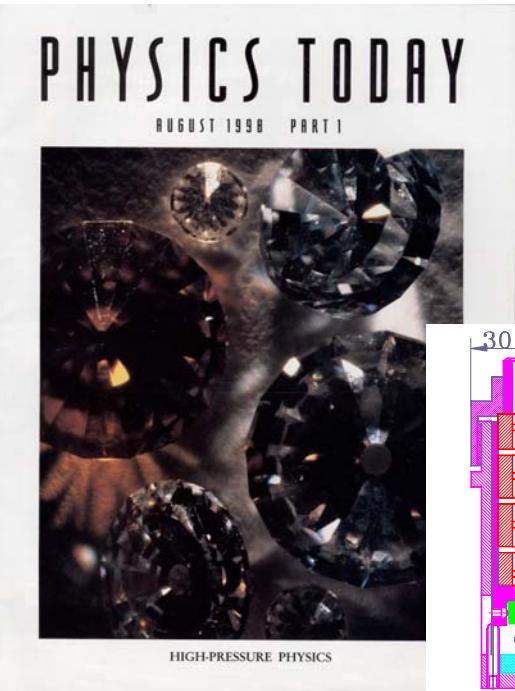
- ELECTRONIC, SEMICONDUCTING, SUPERHARD

Periodic Table of Superconductors

1 H	2 He
4 Be	
Li	
11 Na	12 Mg
19 K	Ca
37 Rb	Sr
Cs	Ba
87 Fr	Ra
22 Ti	Sc
40 Zr	Y
72 Hf	Ta
104 Ru	La
105 Ha	W
106 Unh	Hf
107 Uns	Ta
108 Uno	W
109 Une	Hf
23 V	
41 Nb	
42 Mo	
43 Tc	
44 Ru	
45 Rh	
46 Pd	
47 Ag	
48 Cd	
49 In	
50 Sn	
51 Sb	
52 Te	
53 I	
54 Xe	
6 B	13 Al
7 C	14 Si
8 N	15 P
9 O	16 S
10 F	17 Cl
18 Ne	19 Ar
31 Ga	32 Ge
32 As	33 Se
33 Br	34 Kr
35 Ga	36 Sn
36 As	37 Sb
37 Br	38 Te
38 Kr	39 I
39 Xe	40 At
41 Po	42 Rn
42 At	43 Lu
43 Rn	44 Ce
44 Th	45 Pr
45 Pa	46 Nd
46 U	47 Pm
47 Np	48 Sm
48 Pu	49 Eu
49 Am	50 Gd
50 Cm	51 Tb
51 Bk	52 Dy
52 Cf	53 Ho
53 Es	54 Er
54 Fm	55 Tm
55 Md	56 Yb
56 No	57 Lu

59 Ce	60 Pr	61 Nd	62 Pm	63 Sm	64 Eu	65 Gd	66 Tb	67 Dy	68 Ho	69 Er	70 Tm	71 Yb	72 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

High-Pressure Technology: PLETHORA OF NEW DEVICES



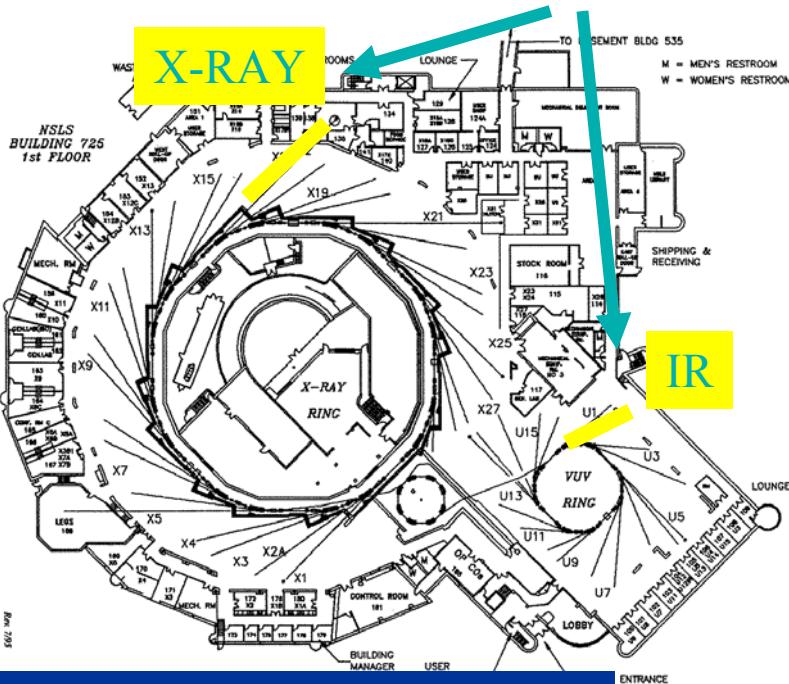
Carnegie Institution

Synchrotron Radiation is Essential

Hard x-ray (>4 keV) to Infrared (to diffraction limit)



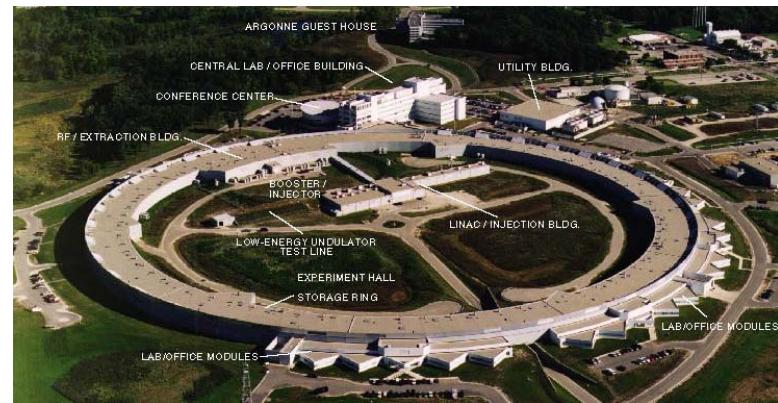
High-Pressure Beam lines



National Synchrotron Light Source
Brookhaven National Laboratory

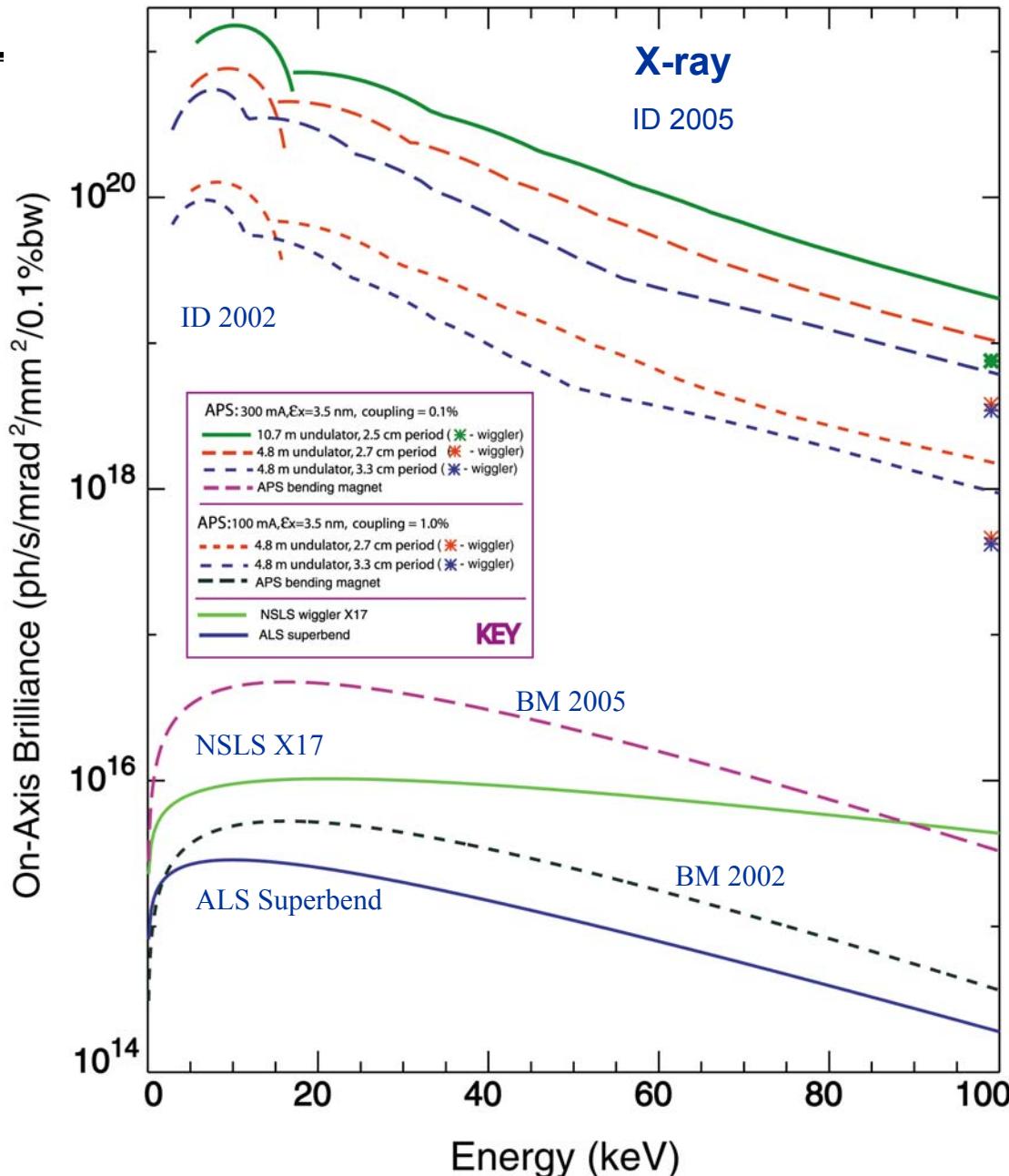
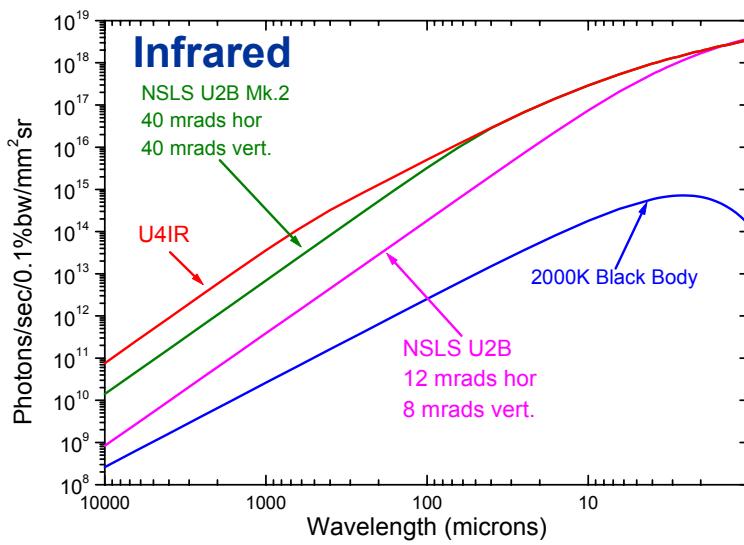
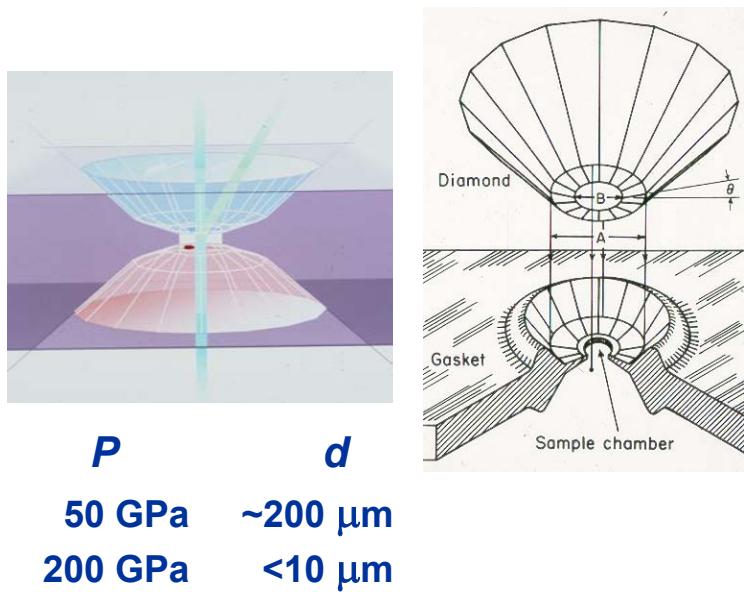
- Three dedicated beamlines (X17B, X17C; U2A)
- Sample preparation laboratory
- Support of other beamlines

- Dedicated High-Pressure facility (HPCAT, Sector 16)
- Other beamlines (Sectors 3, 9, 13)
- Other facilities



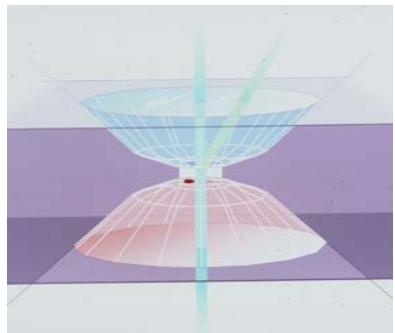
Advanced Photon Source
Argonne National Laboratory

Need for High Brightness Microbeams

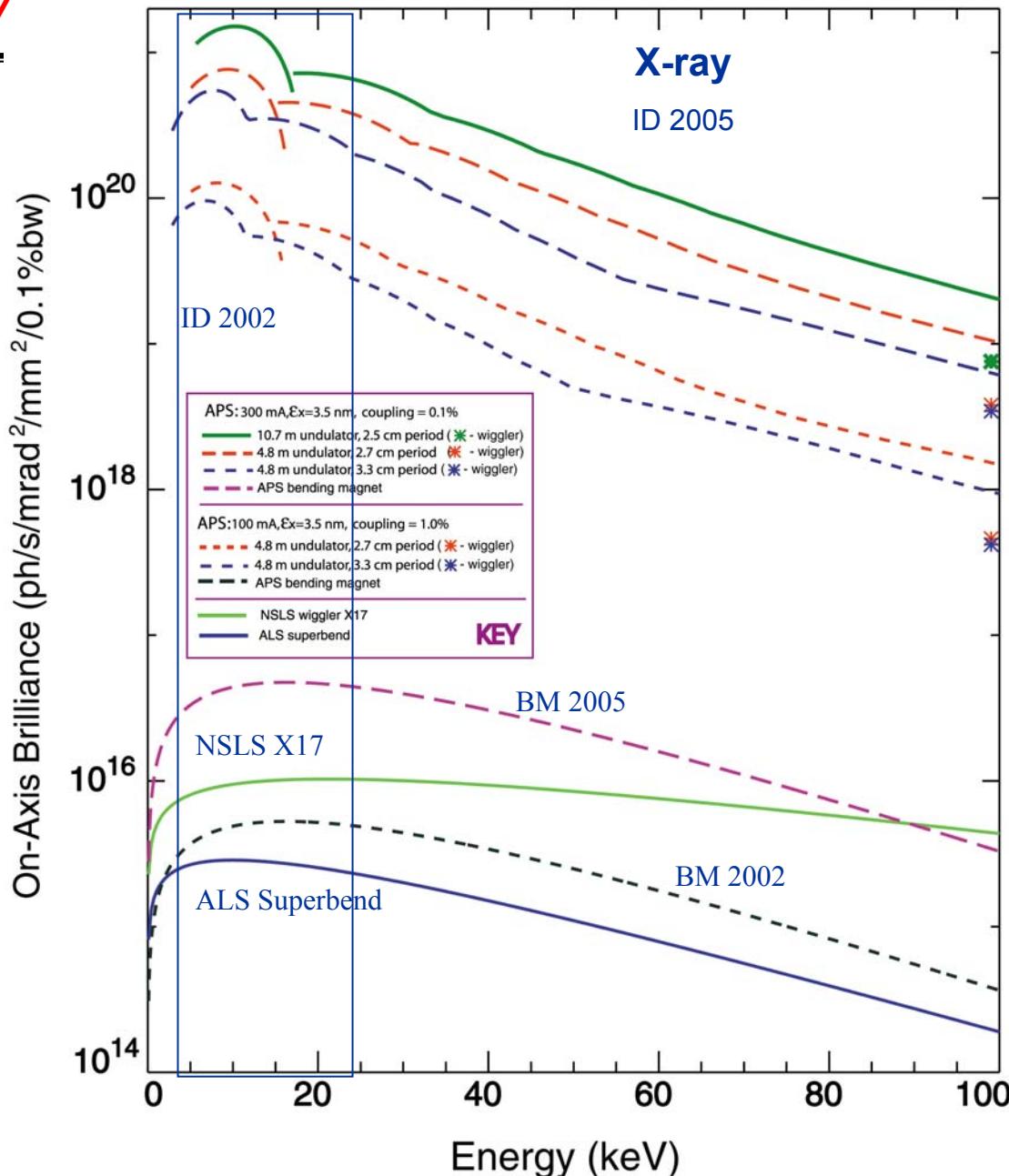
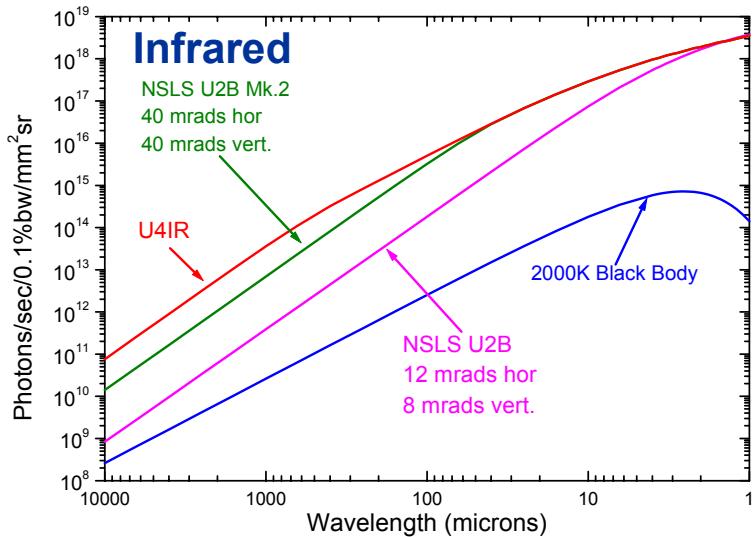
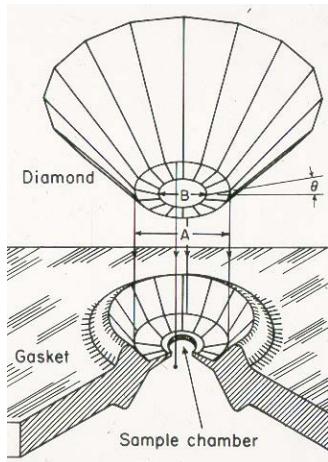


Need for High Brightness Microbeams

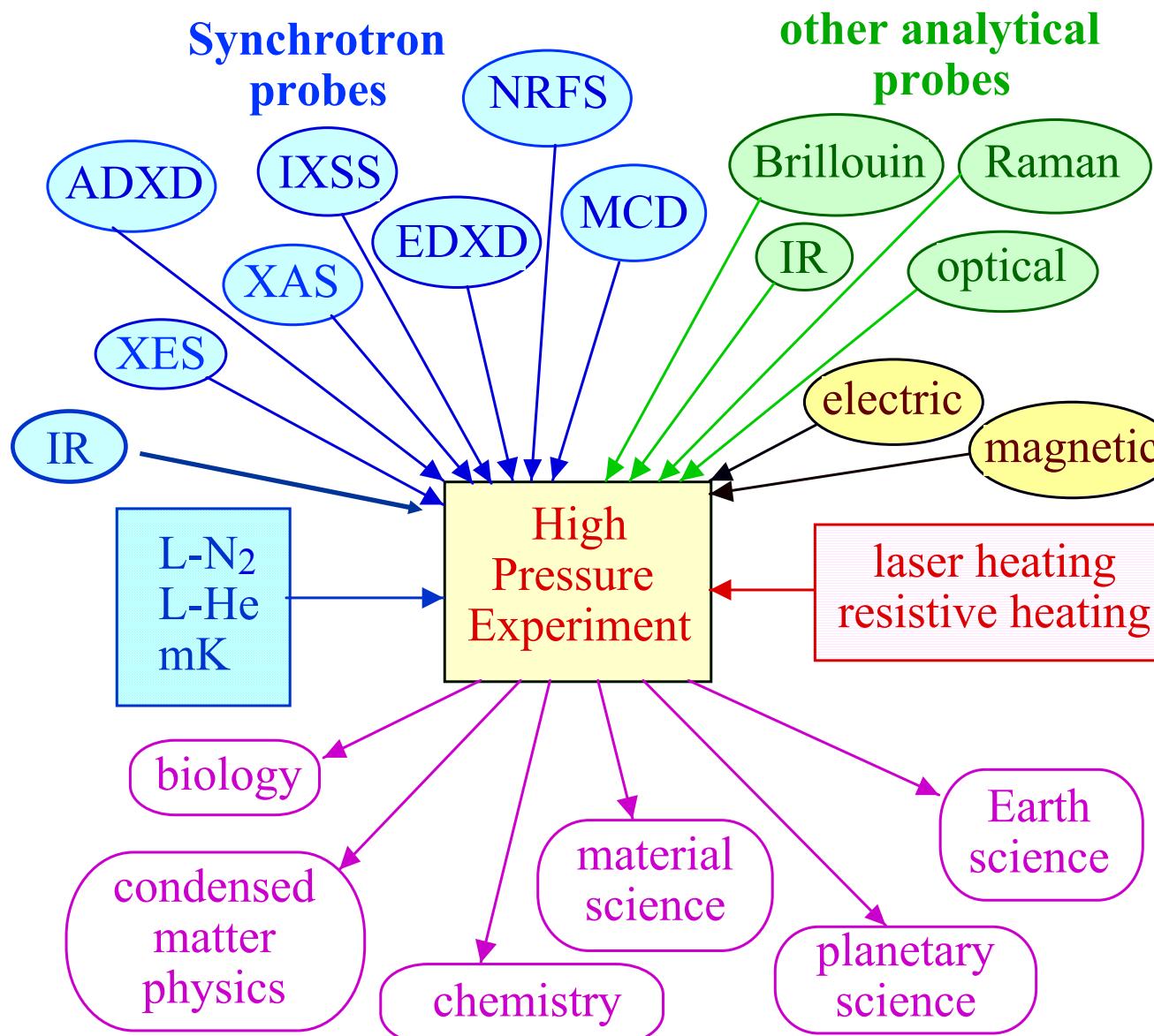
Diamond opaque at >5 eV to ~10 keV



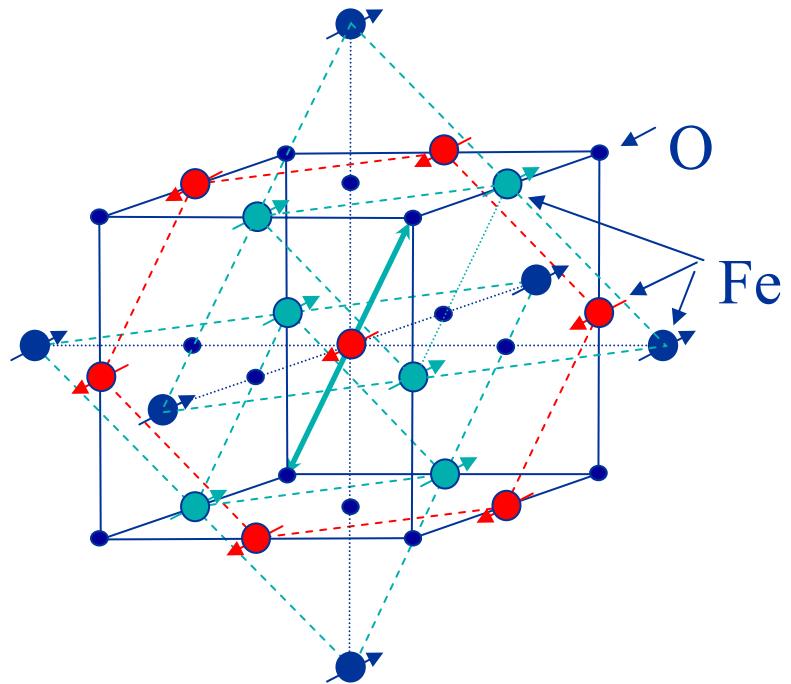
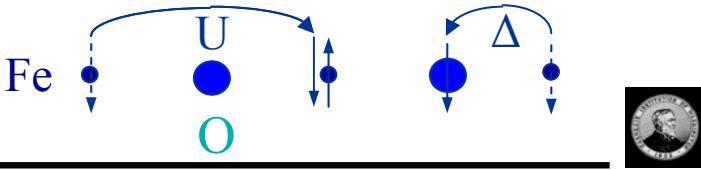
P
50 GPa d
200 GPa $\sim 200 \mu\text{m}$
 <10 μm



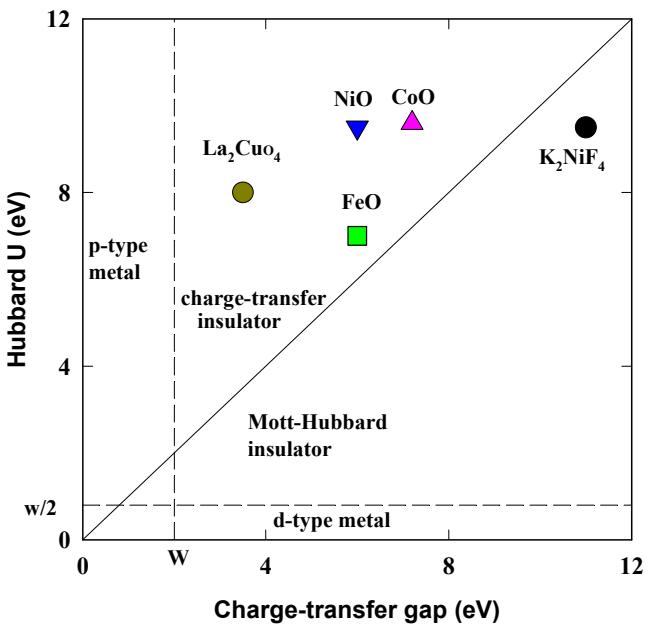
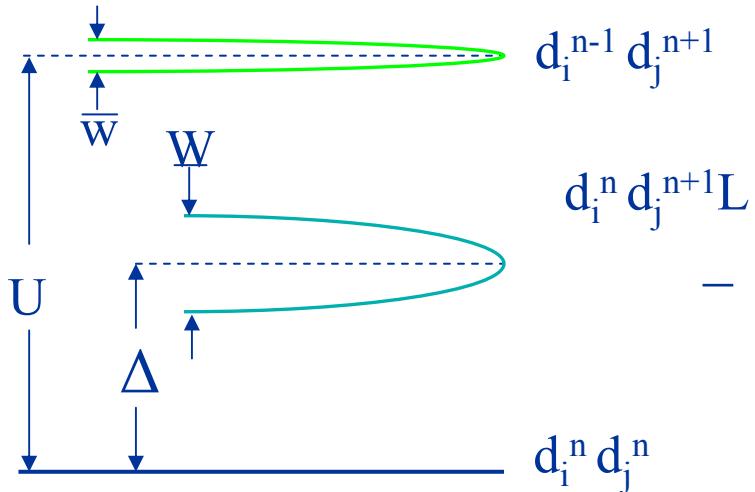
An Integrated Approach



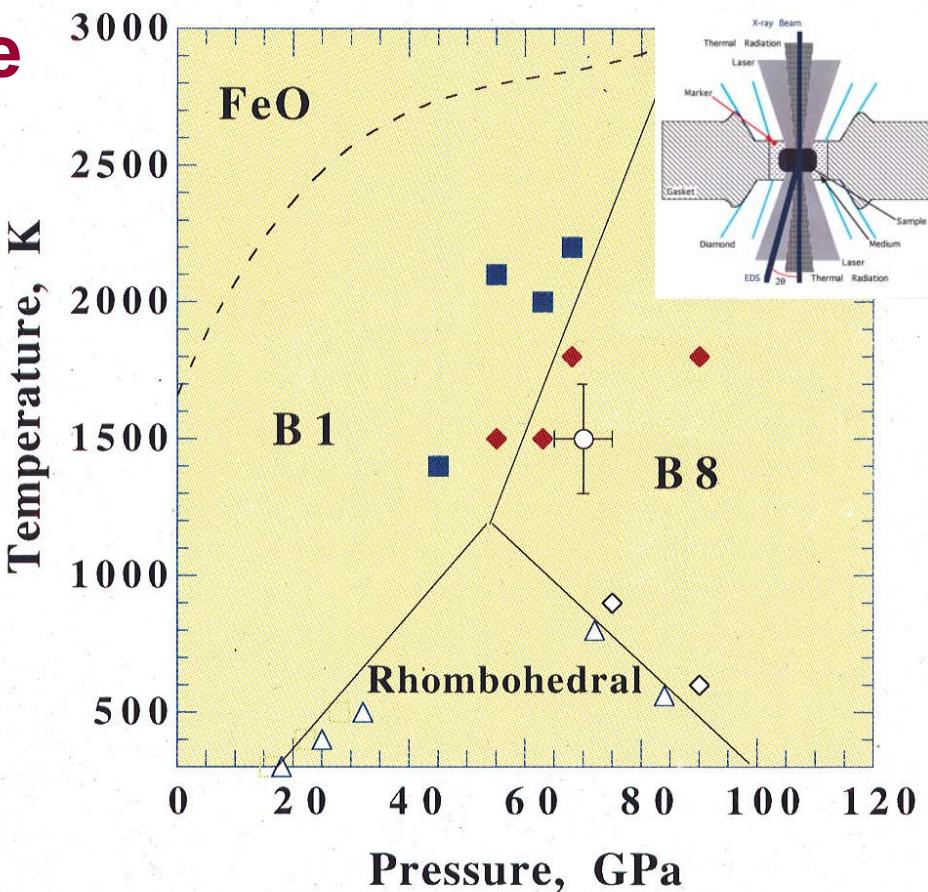
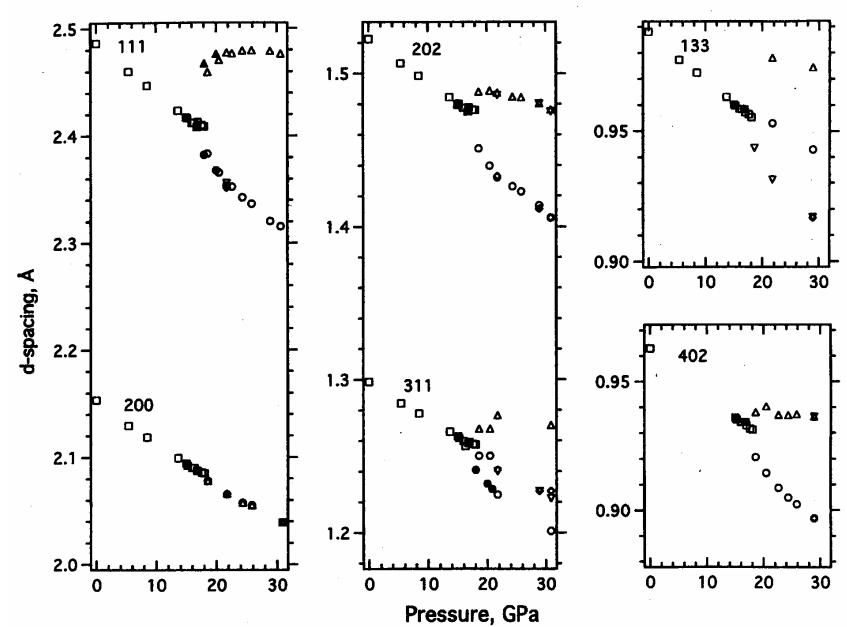
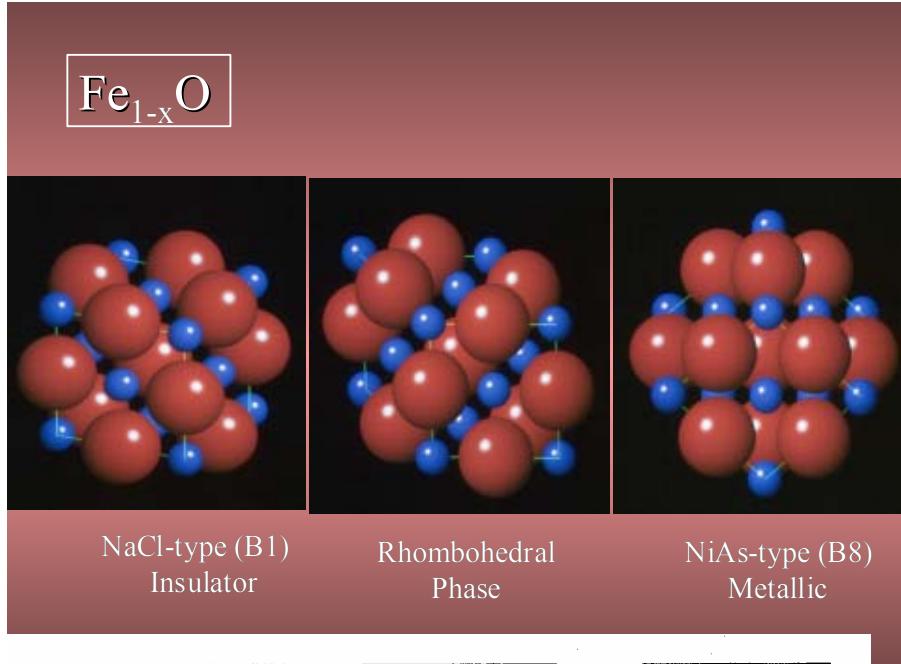
FeO: Prototype Example



- Mott-Hubbard insulator
- Complex high-pressure behavior
- Geophysical implications



FeO: Prototype Example



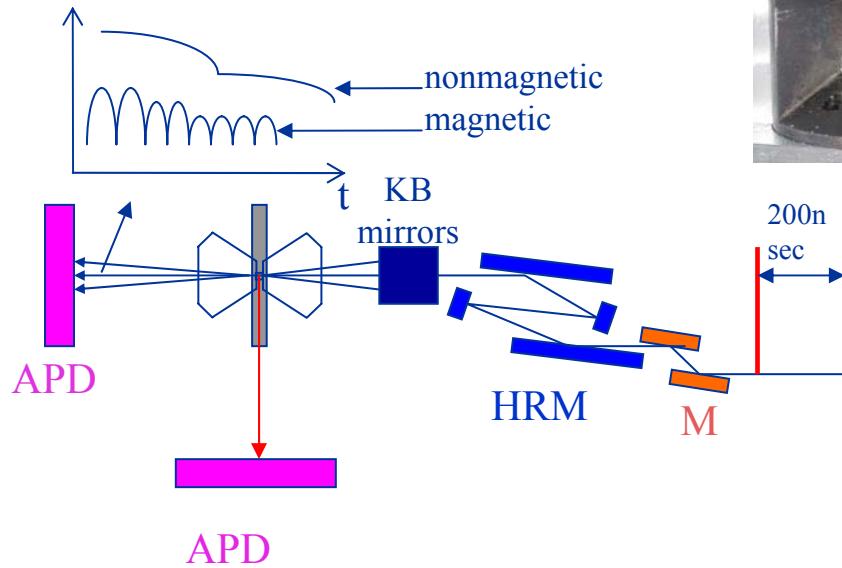
- In situ laser heating/x-ray diffraction identifies high P - T boundaries
[Shen et al., to be published]
- Single-crystal x-ray diffraction (He medium) establishes rhombohedral phase
[Shu et al. (1996)]

Nuclear Resonant Inelastic X-ray Scattering

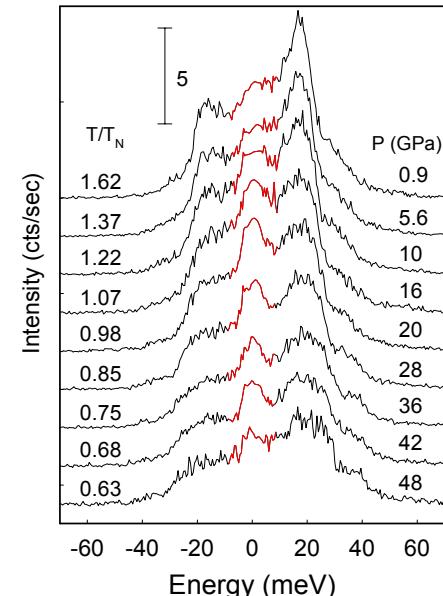
[Struzhkin et al., Phys. Rev. Lett. 87, 25550 (2001)]



Large opening “panoramic” cell

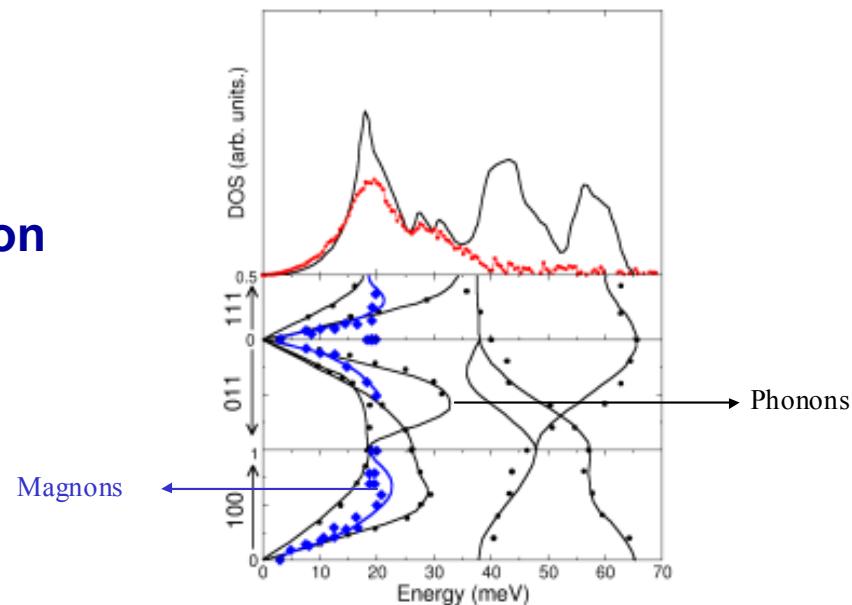


RELATIVE TO MOSSBAUER RESONANCE FOR ^{57}Fe at 14.4 keV



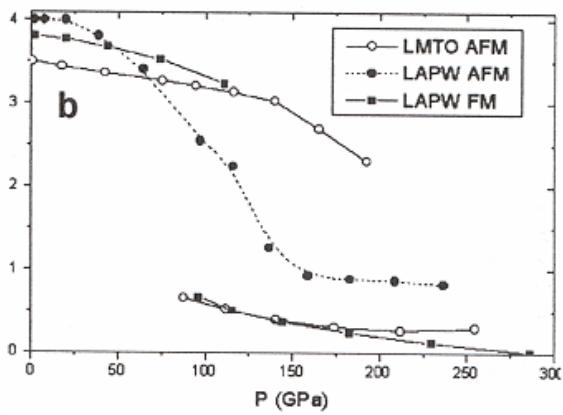
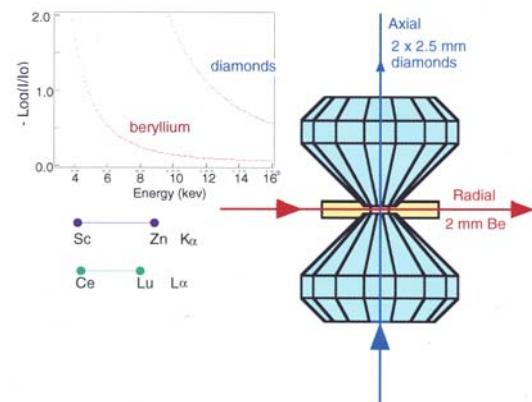
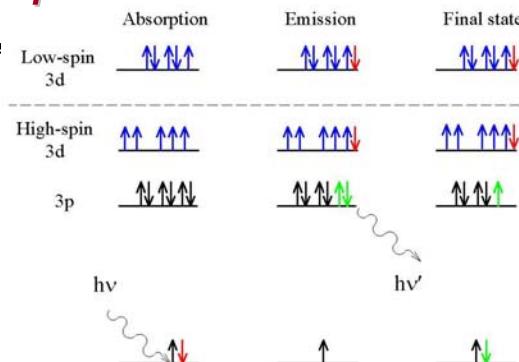
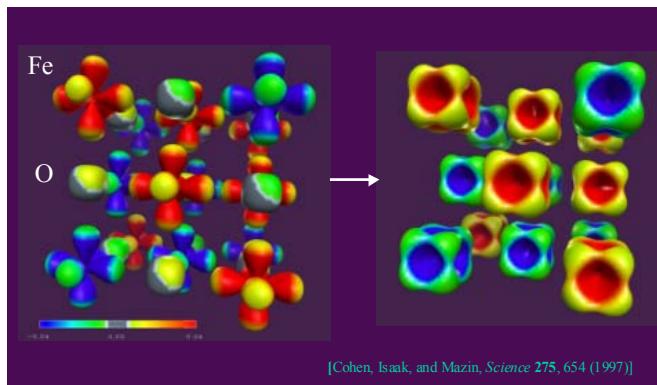
- Strong magnetoelastic coupling
- Origin of rhombohedral displacive transition
- Shear modulus softening

$$\begin{aligned} \mathbf{E} = & \mathbf{B}_1(\alpha_1^2 \mathbf{e}_{xx} + \alpha_2^2 \mathbf{e}_{yy} + \alpha_3^2 \mathbf{e}_{yy}) + \mathbf{B}_2(\alpha_1 \alpha_2 \mathbf{e}_{xy} + \alpha_2 \alpha_3 \mathbf{e}_{yz} + \alpha_1 \alpha_3 \mathbf{e}_{xz}) \\ & + (1/2)\mathbf{C}_{11}(\mathbf{e}_{xx}^2 + \mathbf{e}_{yy}^2 + \mathbf{e}_{zz}^2) + (1/2)\mathbf{C}_{44}(\mathbf{e}_{xy}^2 + \mathbf{e}_{yz}^2 + \mathbf{e}_{zx}^2) \\ & + \mathbf{C}_{12}(\mathbf{e}_{yy}\mathbf{e}_{zz} + \mathbf{e}_{xx}\mathbf{e}_{zz} + \mathbf{e}_{xx}\mathbf{e}_{yy}) \end{aligned}$$



Magnetic Collapse in FeO: *K β* EMISSION SPECTROSCOPY

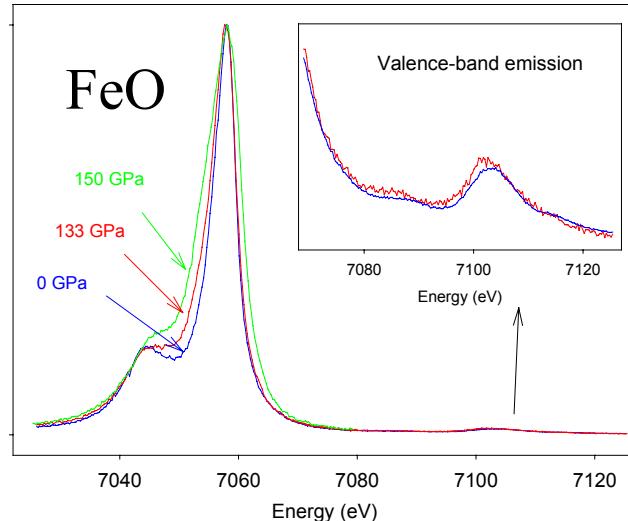
[Badro et al., Phys. Rev. Lett. 83, 4101 (1999)]



**Predicted magnetic collapse
(high-spin/low spin transition)**

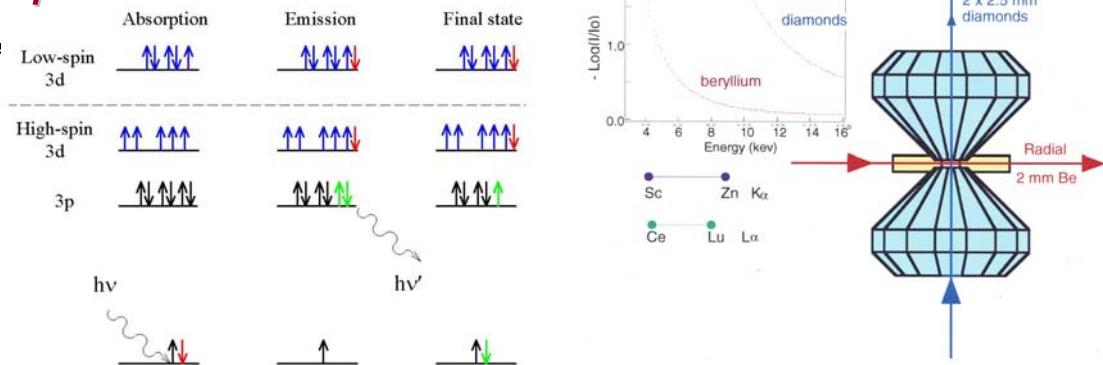
[Cohen et al., Science 275, 654 (1997)]

- X-ray transparent Be gasket
- Rowland circle spectrometer (0.5 eV)
- Focused x-ray beams (10 μm spots)

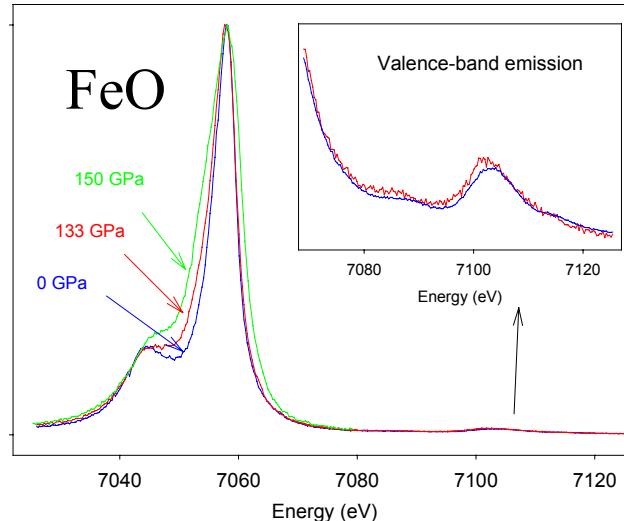
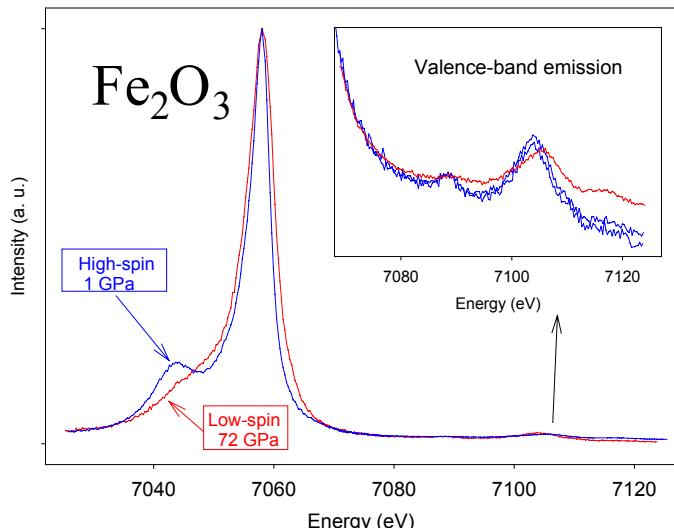


Magnetic Collapse in FeO: *K β* EMISSION SPECTROSCOPY

[Badro et al., Phys. Rev. Lett. 83, 4101 (1999)]



- X-ray transparent Be gasket
- Rowland circle spectrometer (0.5 eV)
- Focused x-ray beams (10 μm spots)



Insulator-Metal Transition in FeO

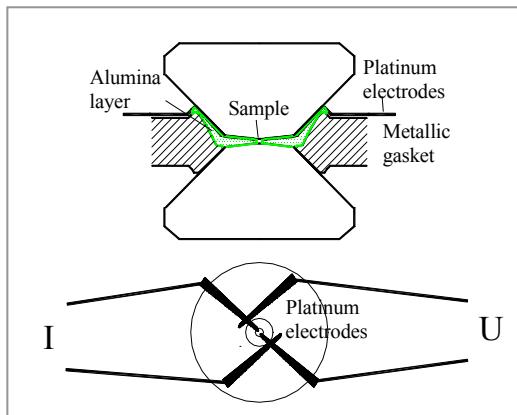


[Eremets et al., to be published]

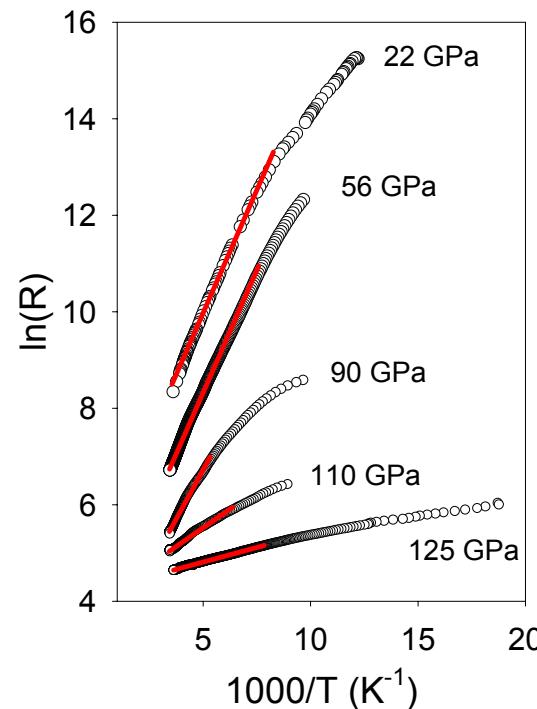
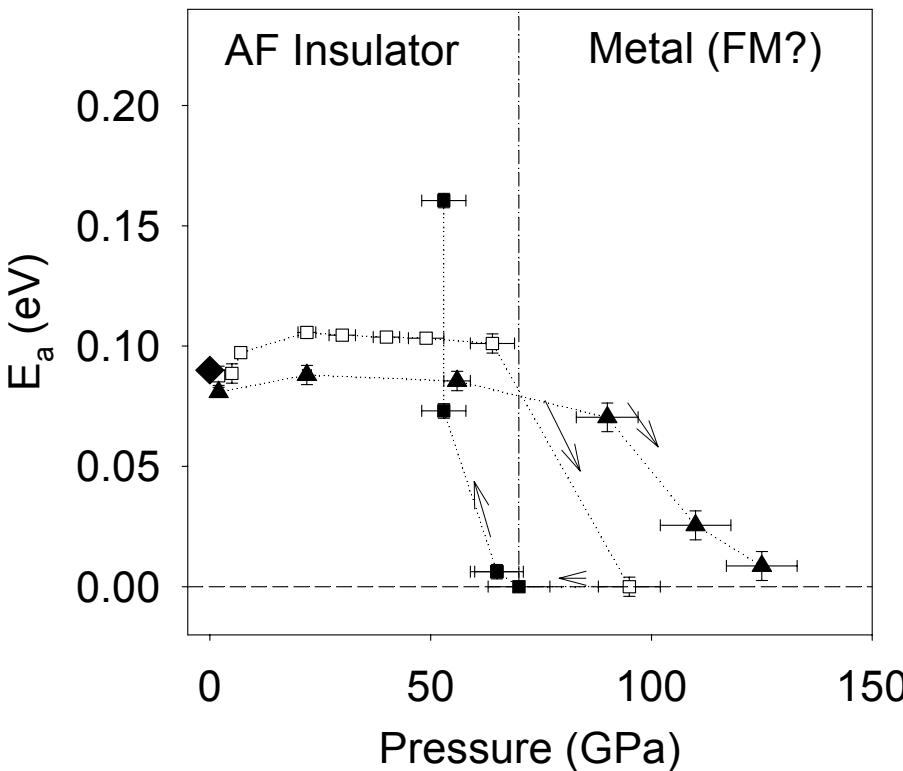
41 GPa



113 GPa

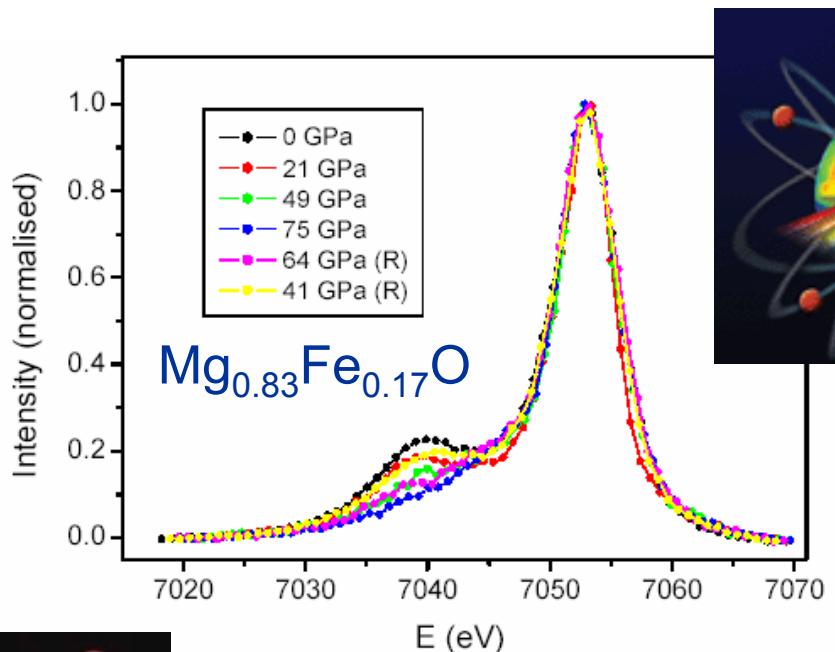


- $\sigma(\omega)$ from IR reflectivity
- Higher pressure

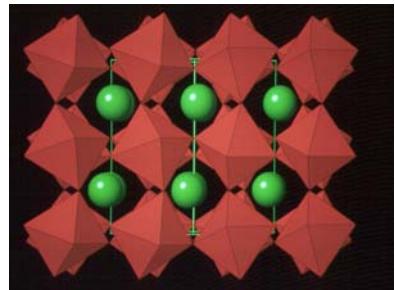
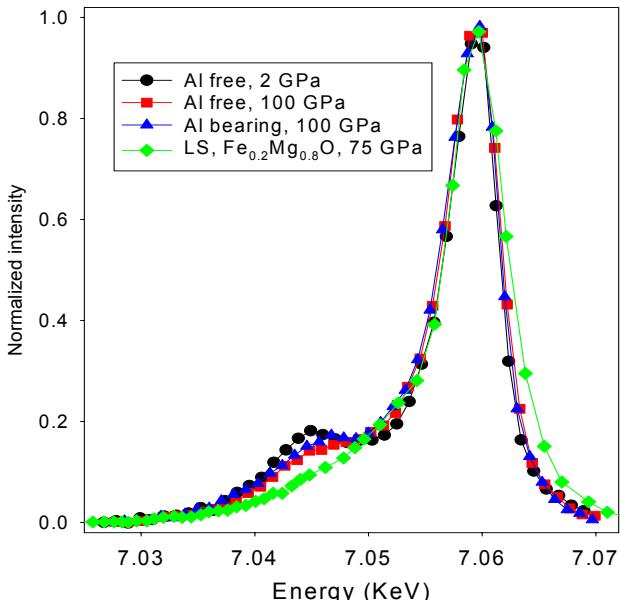
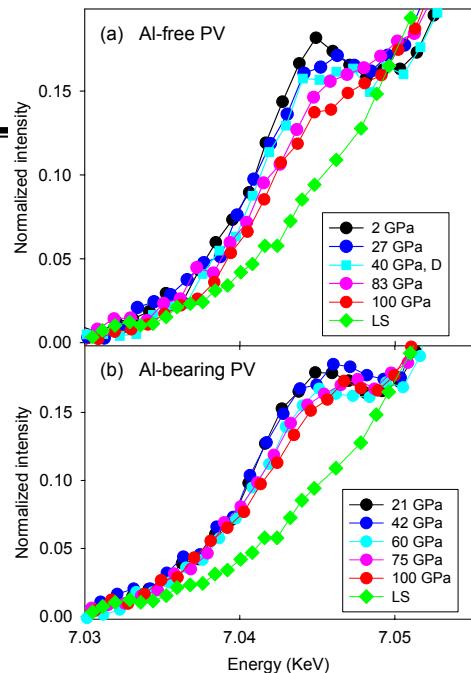
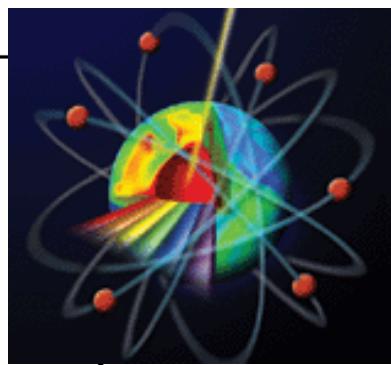
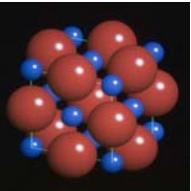


Implications for the Earth

LOW-SPIN Fe IN THE DEEP MANTLE



[Badro et al., *Science* 300, 789 (2003)]



- $(Mg,Fe,Al)SiO_3$ perovskite: most abundant mineral in planet
- High-spin/low-spin transition ~ 100 GPa

[Li et al., *Science*, submitted]

Carnegie Institution

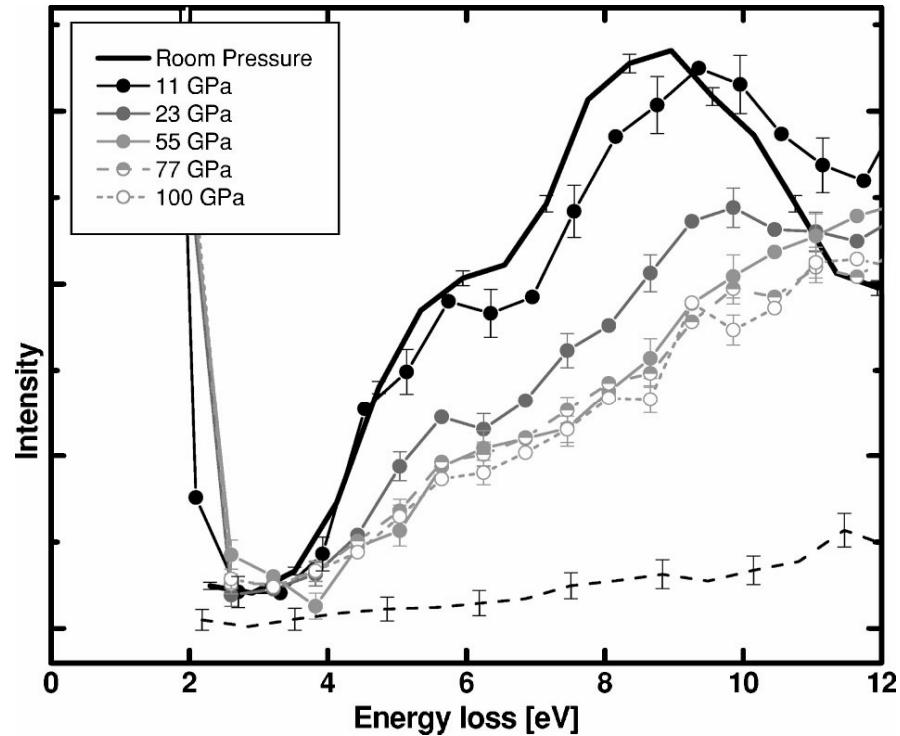
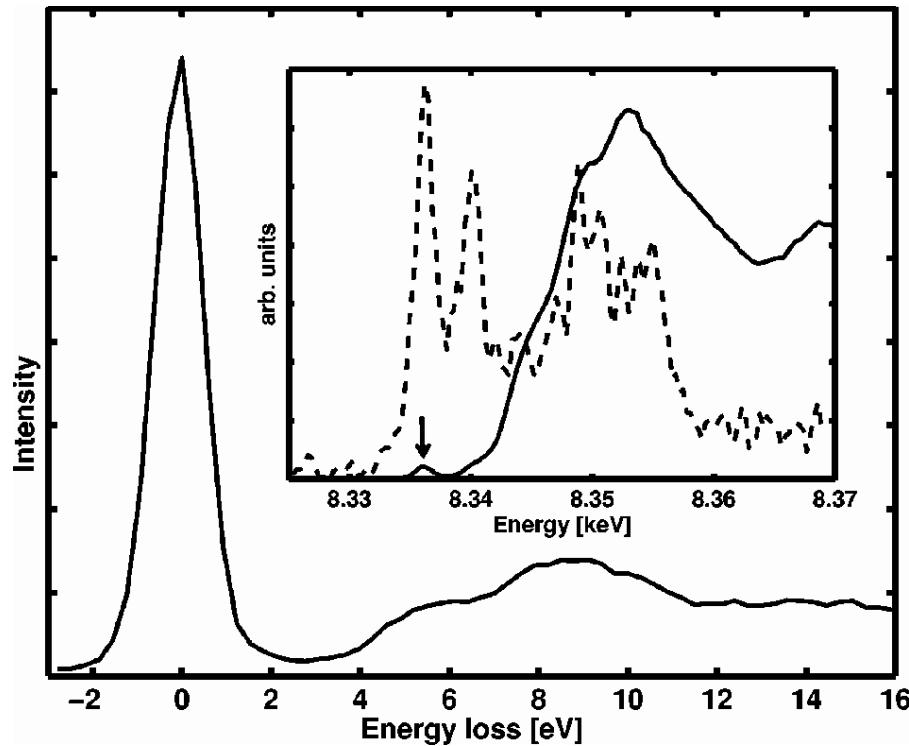
Charge Transfer in NiO: RIXS TO 100 GPa

[Shuka et al., Phys. Rev. B 67,
081101 (2003)]



- Zero-pressure measurements

[Kao et al., Phys. Rev. B 54, 16361 (1996)]



- Be gasket technique
- ESRF (ID16), $\Delta E = 1.4$ eV
- Marked increase in band dispersion

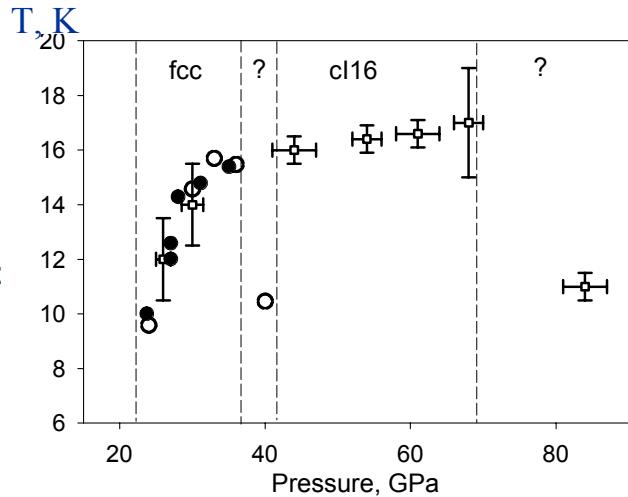
➤ Accurate structure determination
➤ Need for hydrostatic conditions

Novel Superconductors at High Pressure

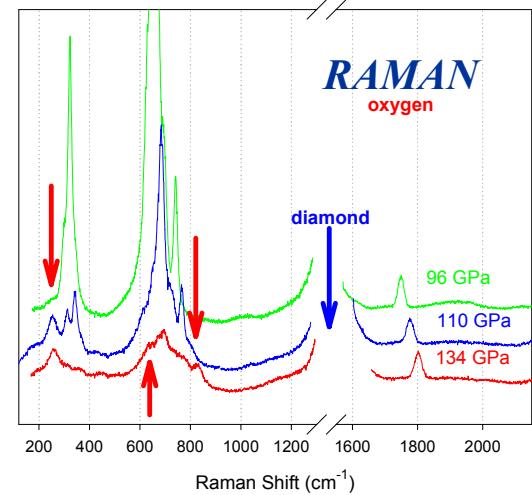


Lithium
*High- T_c ->
“molecular”
metal*

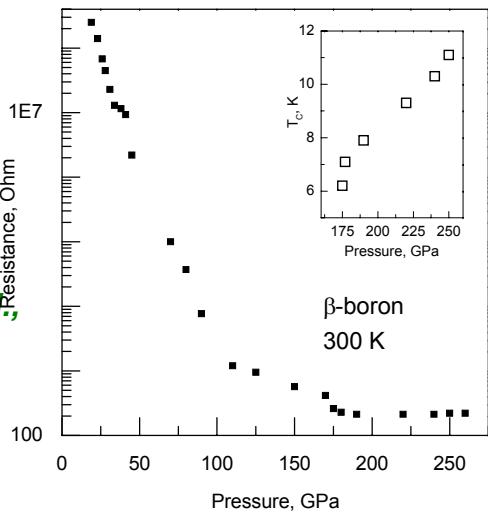
[Neaton & Ashcroft
(2001); Shimizu
et al. (2002);
Struzhkin et al.
(2002); Hanfland
et al. (2002)]



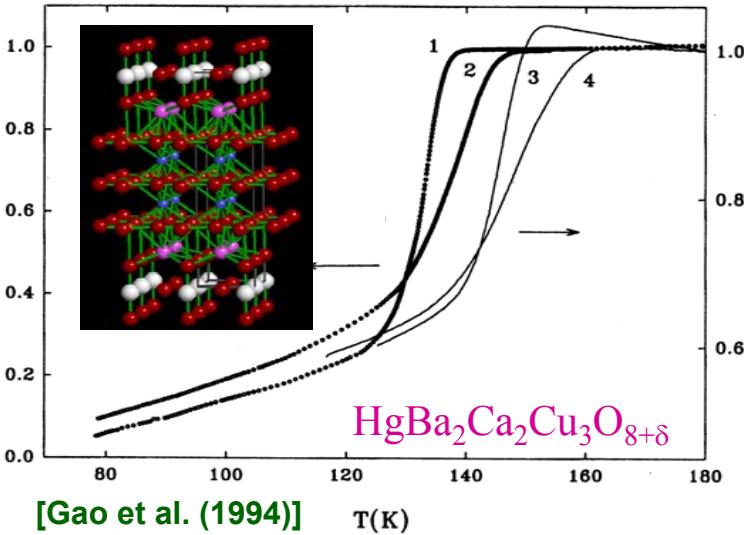
**Oxygen
molecular
superconductor**
[Shimizu et al.
(1998); Weck et al.
(2002); Goncharov
et al., in press]



Boron
 $T_c = 11\text{ K}$
250 GPa
[Eremets et al.,
(2001)]



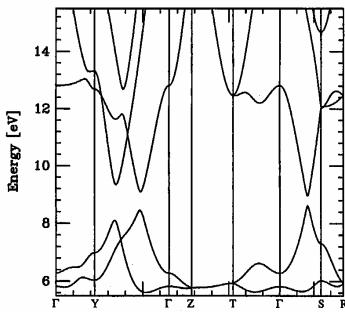
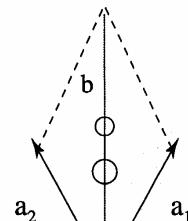
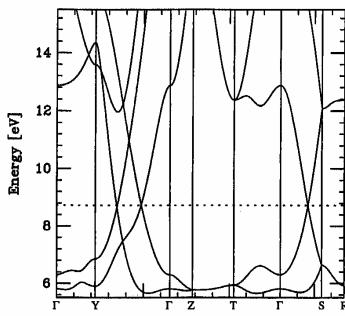
Cuprates
*Highest T_c :
164 K
at 30 GPa*



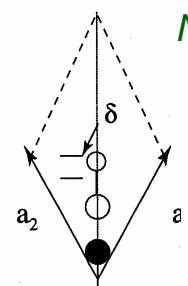
[Gao et al. (1994)]

PRESSURE-INDUCED TRANSFORMATIONS IN LITHIUM

Theoretical Predictions and X-ray Diffraction

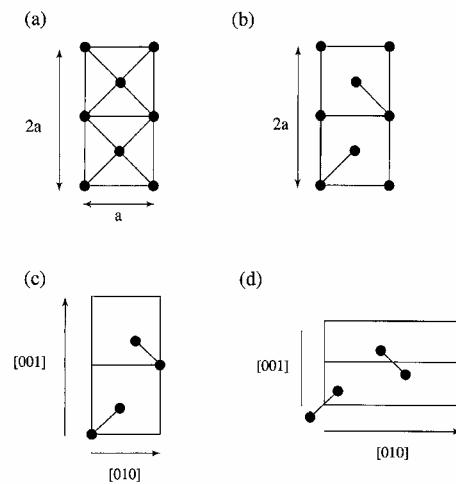


[Neaton & Ashcroft,
Nature **400**, 141 (1999)]

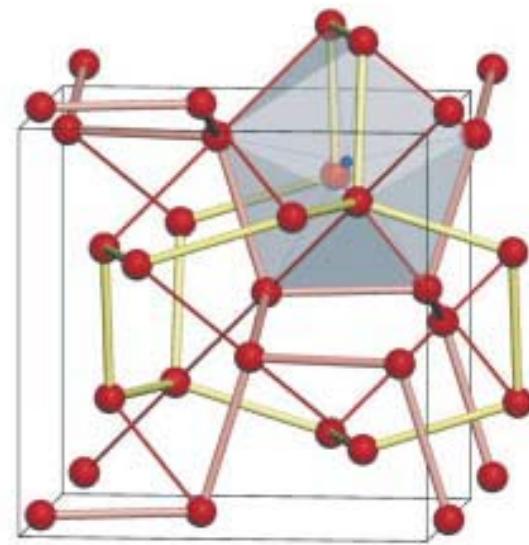


THEORY: Dense Lithium
as a Molecular Solid:
**METAL-INSULATOR AND
PAIRING TRANSITIONS,
SUPERCONDUCTIVITY**

[see also, Christensen & Novikov,
Phys. Rev. Lett. **86**, 1861 (2001)]



[Hanfland et al., *Nature* **408**, 174 (2000)]



45 GPa

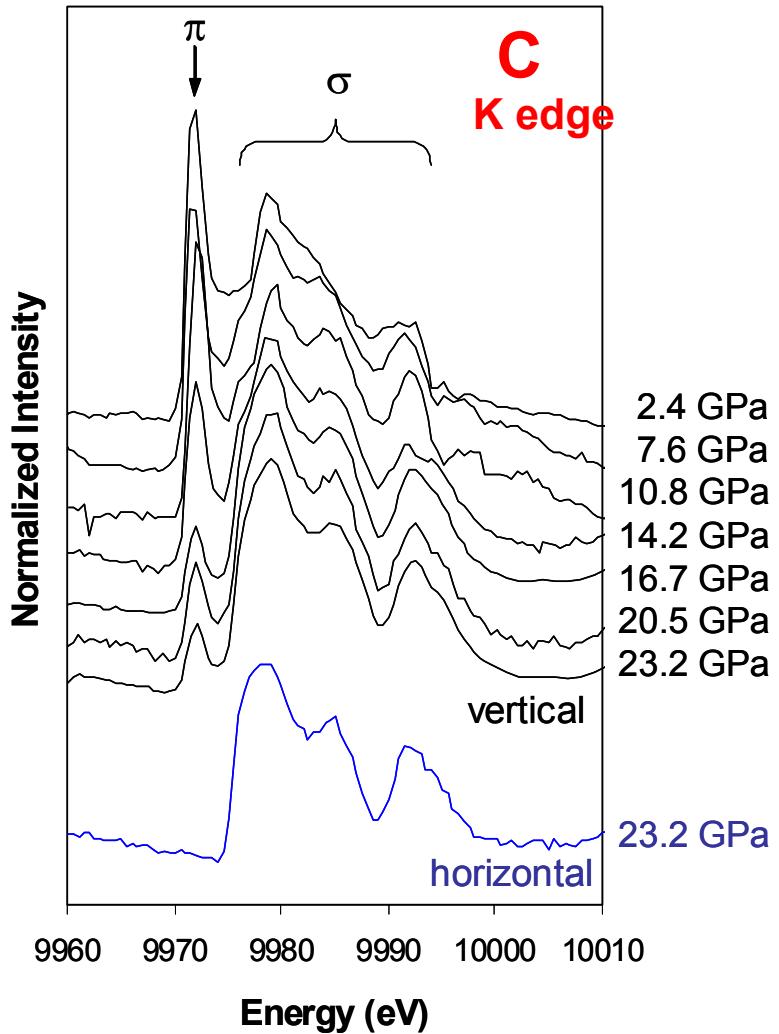
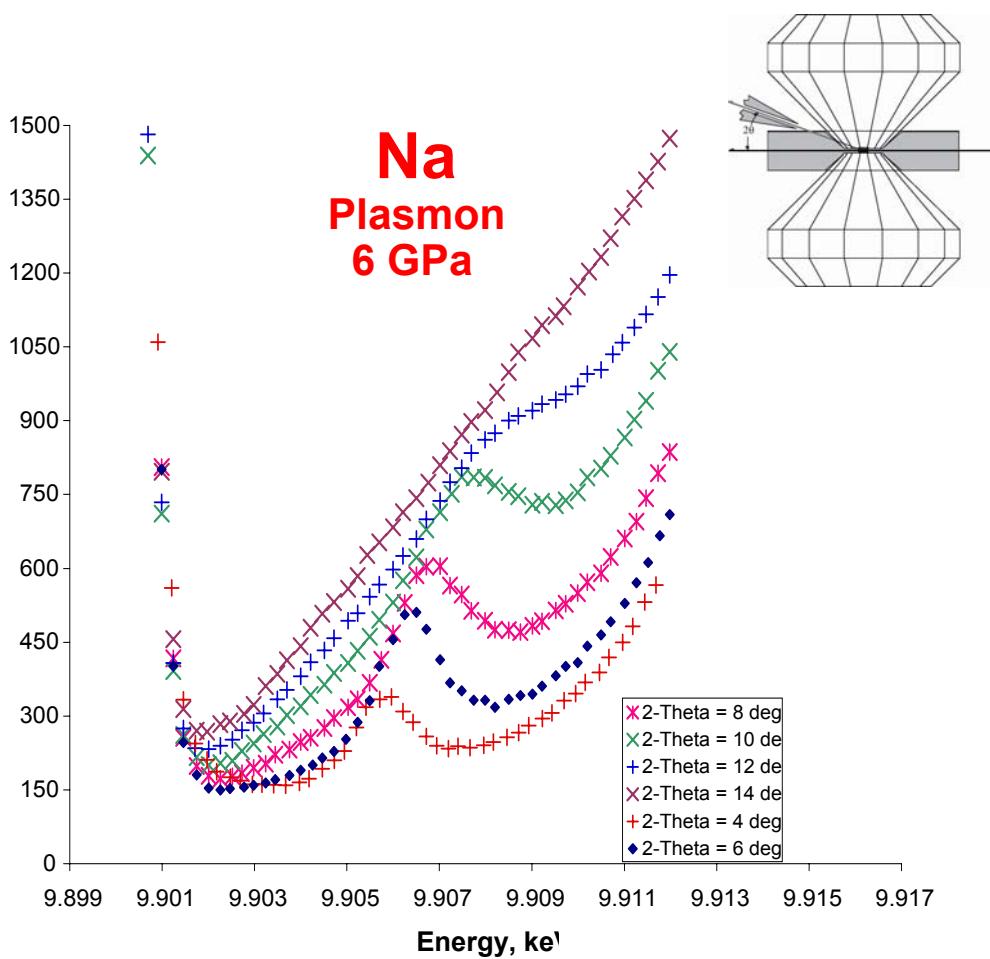
- Cubic 16 atom cell polymorph
- New structure type
- Predicted to be a semimetal, consistent with IR data

[Struzhkin et al., *Bull. Am. Soc.* **44**, 1489 (1999)]

IXS OF 'SIMPLE' ELEMENTS

Feasibility Studies

[W. Mao, et al. *Science*, submitted]



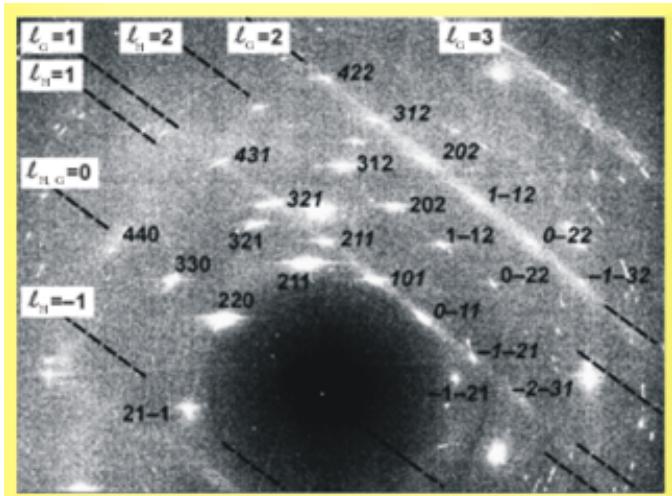
- Tune r_s to critical value for exact expression of $S(q, \omega)$ for the electron gas

- Bonding changes in 17 GPa transition in graphite

“Weird” Metals

Bi-III

Incommensurate host-guest structures in group-V elements: structure solution from combined powder and single-crystal diffraction data

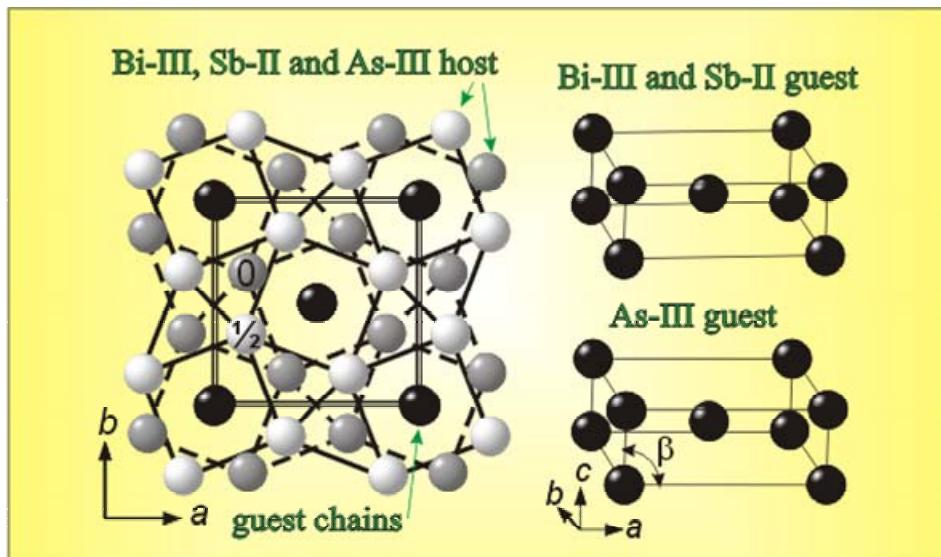


[McMahon, Degtyareva & Nelmes,
Phys. Rev. Lett. 85, 4896 (2000);
Degtyareva et al., to be published]

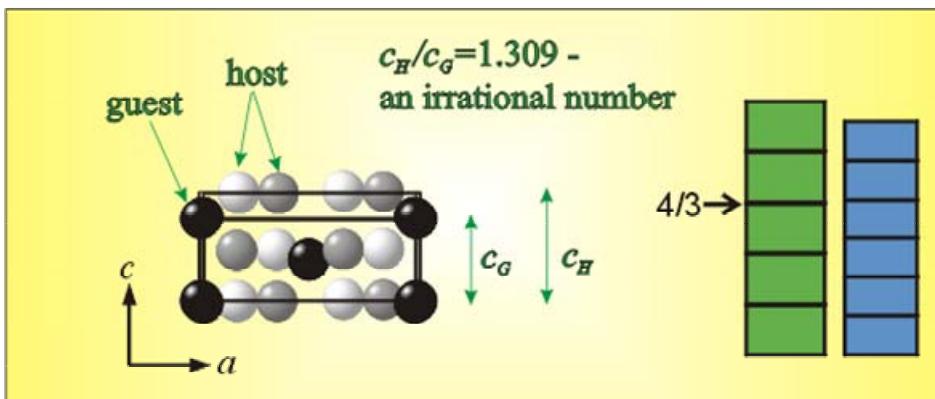
Cs, Rb, Ga, Se, Te

Crystal structure of group-V elements

composed of two interpenetrating ‘host’ and ‘guest’ components that are incommensurate with each other along the c -axis.



The host structure forms channels along the c -axis, occupied by chains of guest atoms. The chains are partially disordered, causing diffuse scattering.



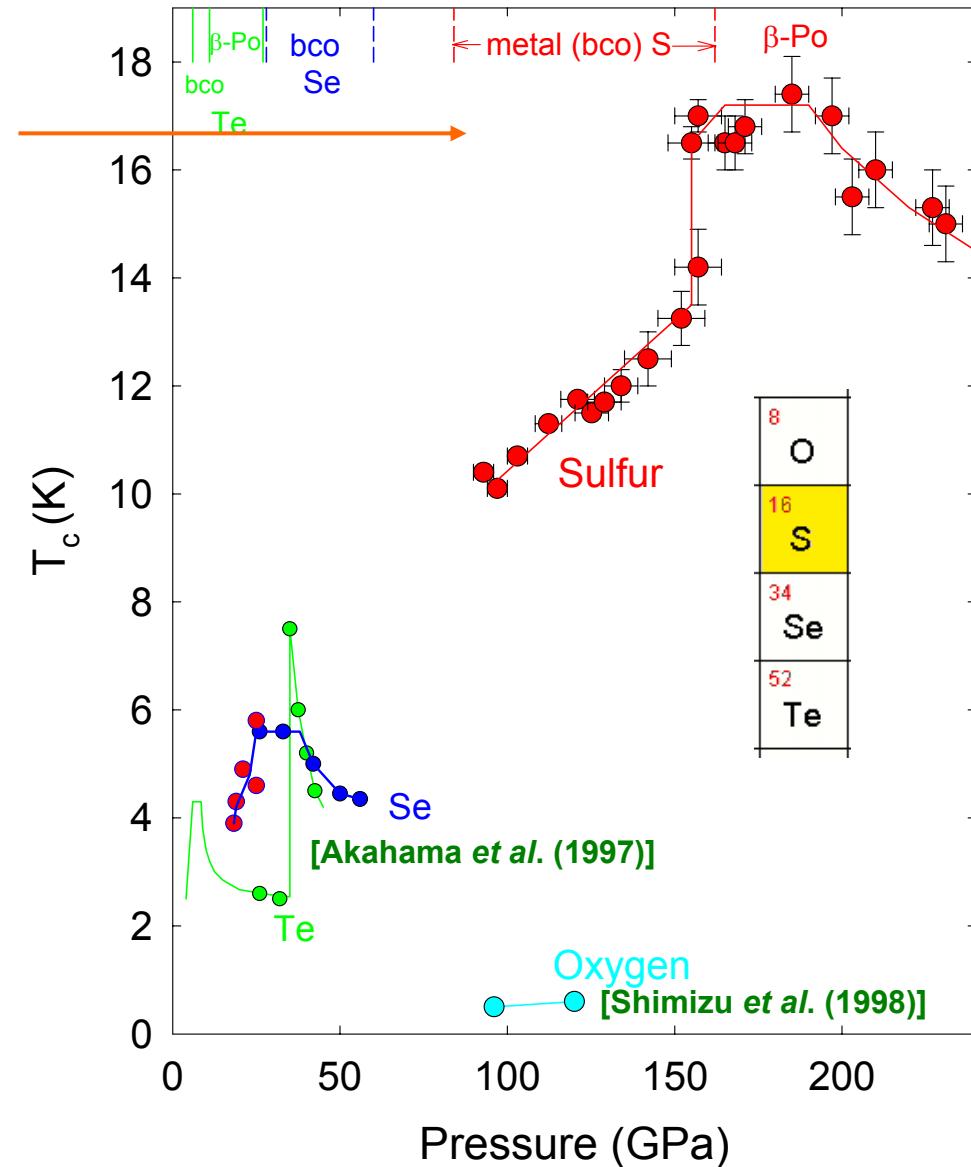
Superconductivity in the Chalcogens

[Gregoryanz et al., Phys. Rev. B 65, 06504 (2002)]



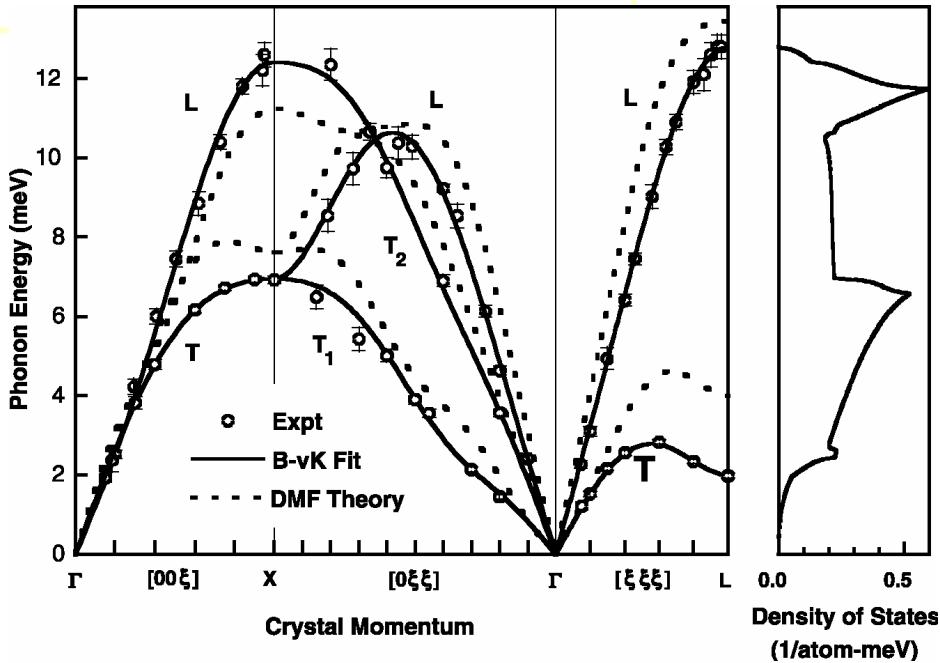
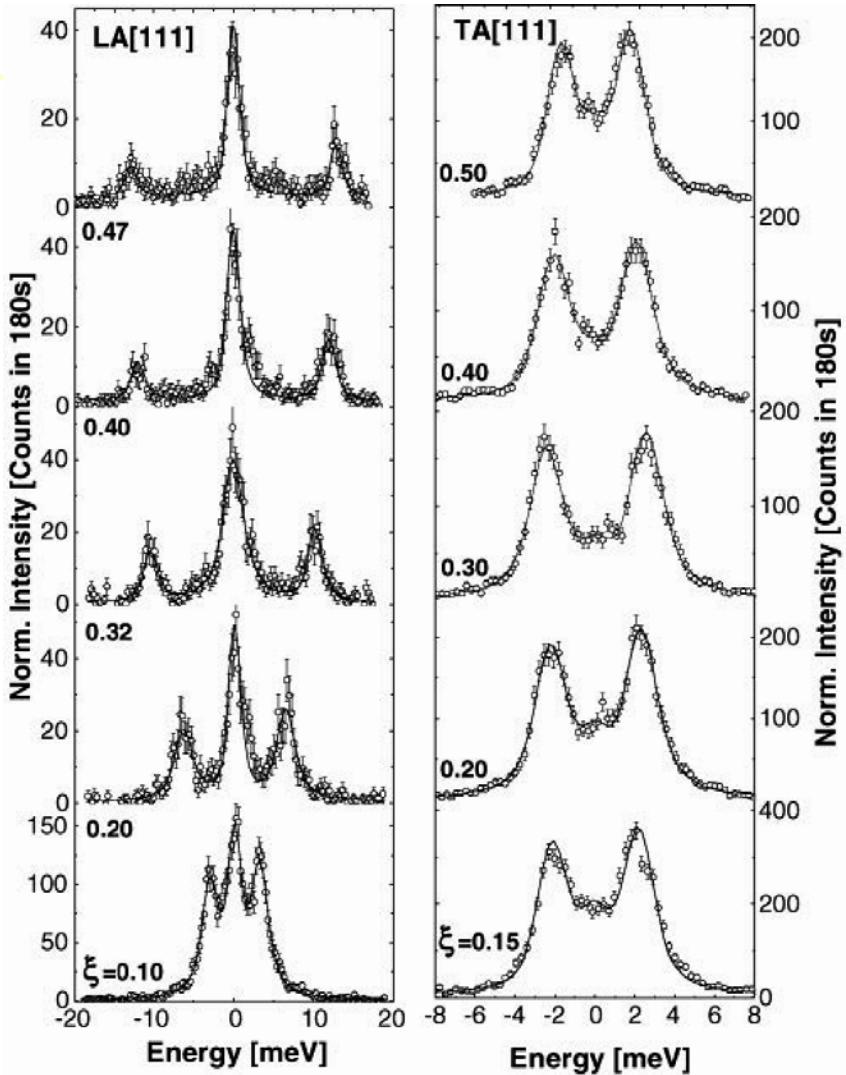
MAGNETIC
SUSCEPTIBILITY
TECHNIQUE

- **Structures by single-crystal/
powder diffraction
(host-guest, incommensurate
– Se, Te)**
- **Electronic structure/phonons
by IXS**



Phonon Dispersion in Plutonium: ZERO PRESSURE IXS

[Wang et al., Science
301, 1078 (2003)]



- Origin of anomalous properties of δ -phase
- IXS (ESRF) on oriented grains
- Good agreement with theory (LDA+U)

[Dai et al., Science 300, 953 (2003)]

➤ Extend to other high pressure



VOLUME 78, NUMBER 1

PHYSICAL REVIEW LETTERS

1 JANUARY 1997

High Temperature Superconductivity in Metallic Hydrogen: Electron-Electron Enhancements

C. F. Richardson¹ and N. W. Ashcroft^{1,2}

¹*Laboratory of Atomic and Solid State Physics and Materials Science Center, Cornell University, Ithaca, New York 14853-2501*

²*New Zealand Institute for Industrial Research, Lower Hutt, New Zealand*

(Received 28 August 1996)

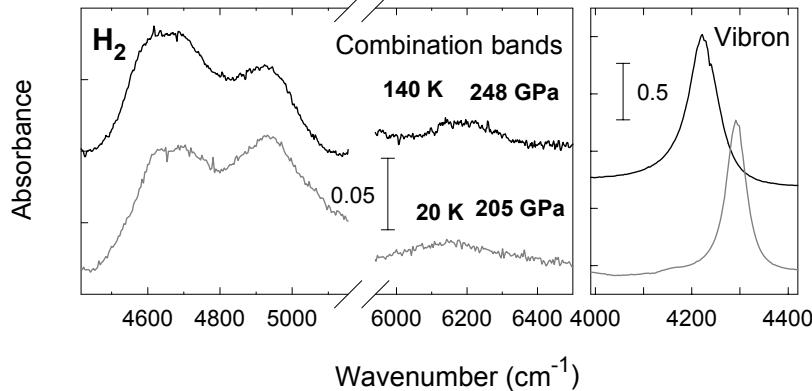
We investigate the possibility of superconductivity in a dense phase of hydrogen which becomes metallic while retaining diatomic character. Correlated fluctuations between electrons and holes in the ensuing band-overlap state can lead to significant enhancements in the transition temperature (compared with monatomic phases) principally through a reduction in the associated Coulomb pseudopotential. The effective electron-electron interaction is determined by a method which treats electrons and phonons on an equivalent footing, an approach which confirms that monatomic phases also remain candidates for high temperature superconductivity. [S0031-9007(96)01982-5]

PACS numbers: 74.10.+v, 71.30.+h, 71.45.Gm, 74.62.-c

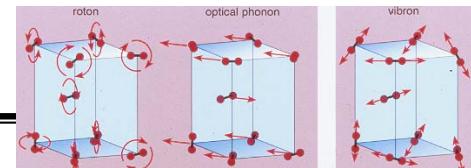
Synchrotron IR Spectroscopy Of Dense Hydrogen



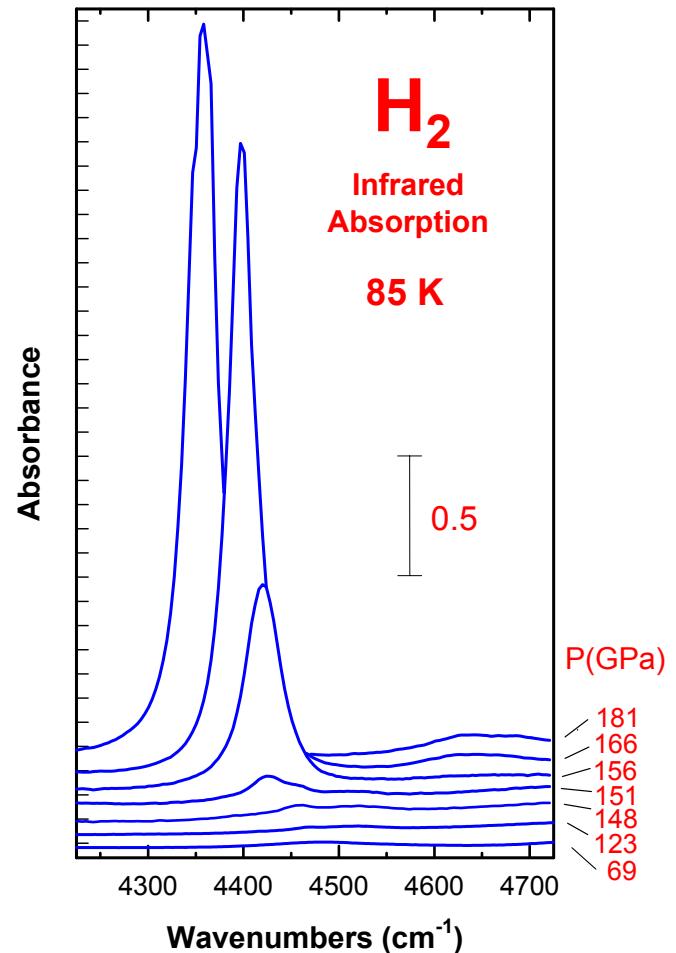
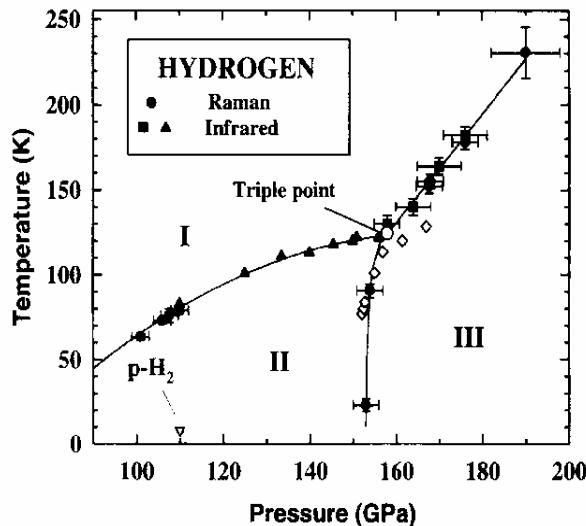
- ‘Charge transfer’ state at 150 GPa



[Goncharov
et al. (2001)]

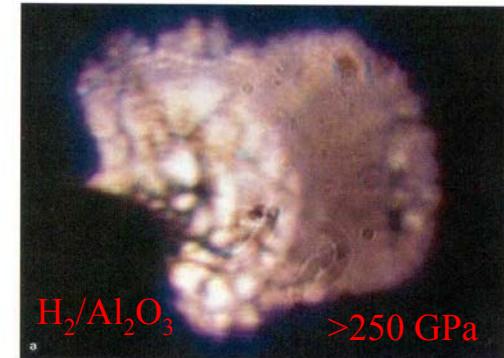
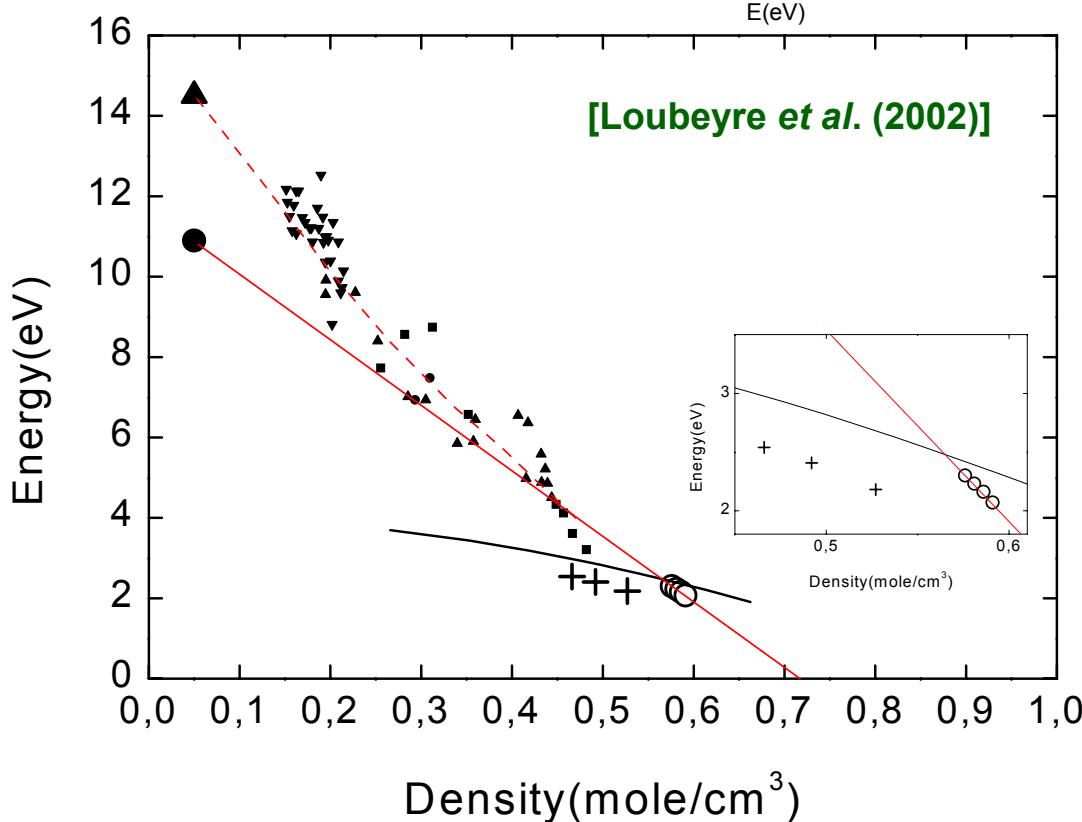
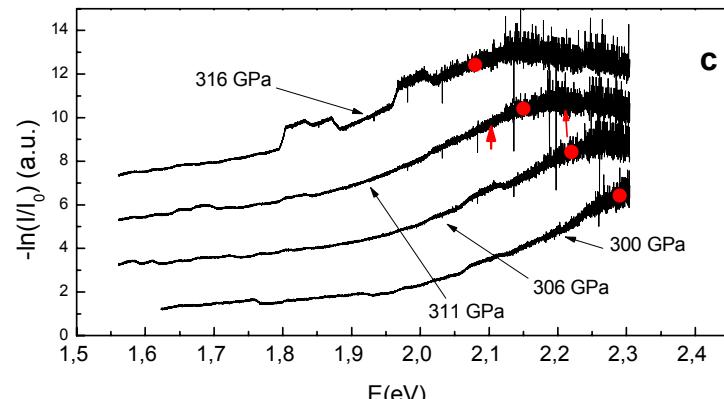


- Phase diagram

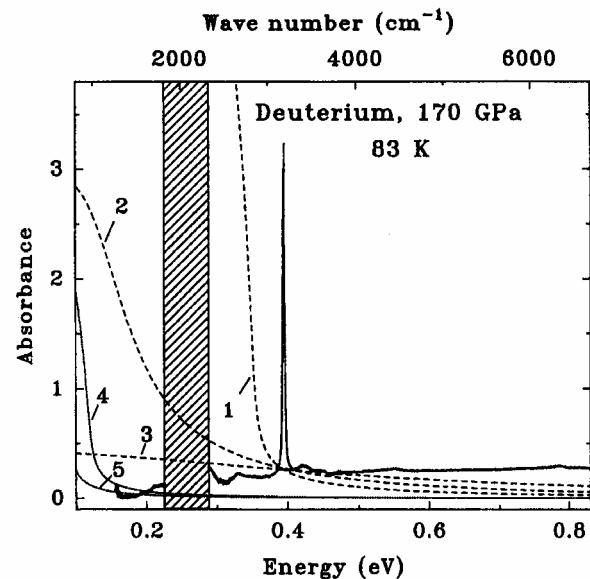


[Hanfland *et al.* (1993); Hemley *et al.* (1994)
see also Chen *et al.* (1995) for D₂]
Carnegie Institution

Optical/Infrared Absorption of Hydrogen at Very High Pressures

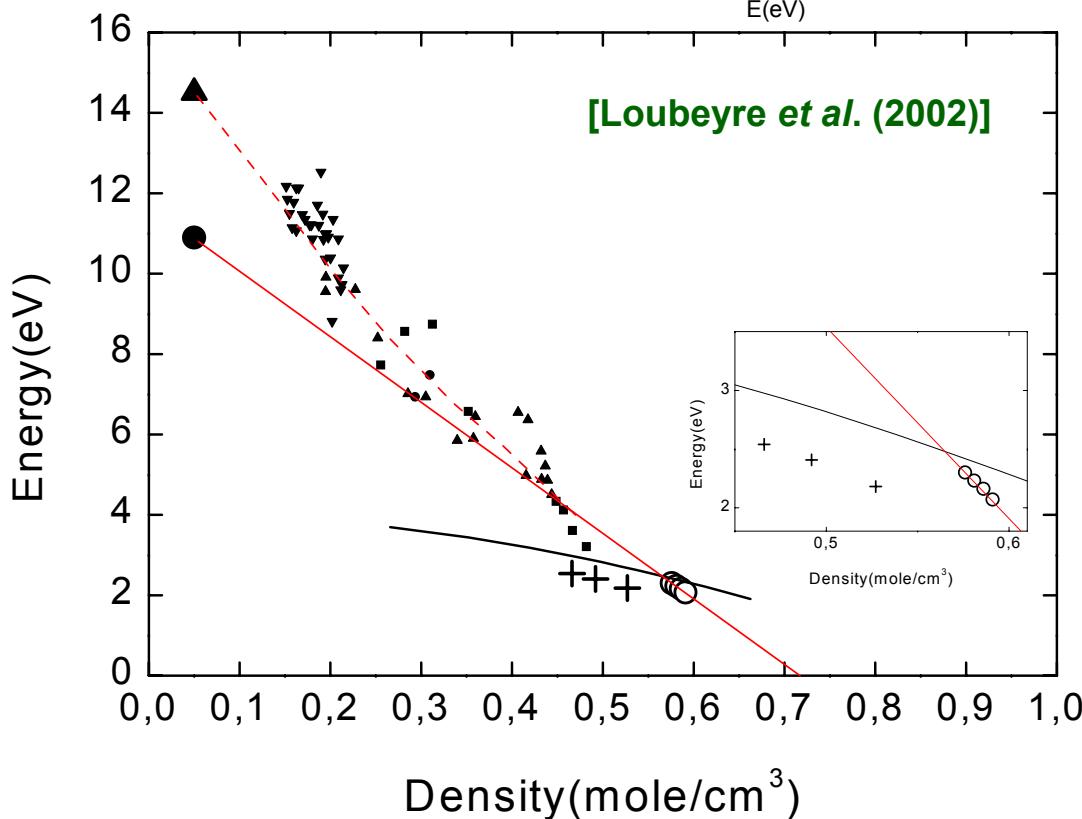
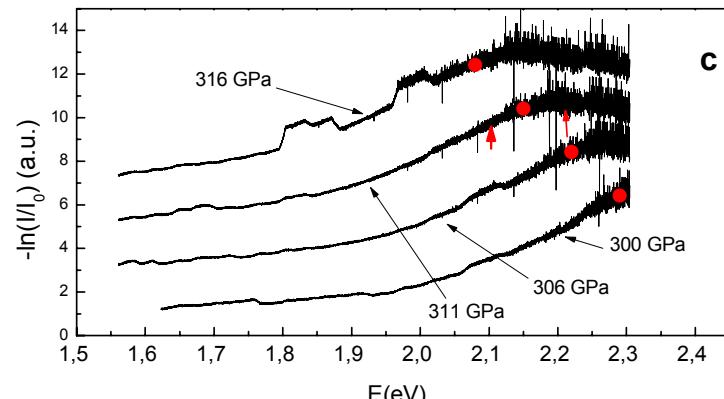


[Mao & Hemley (1989)]

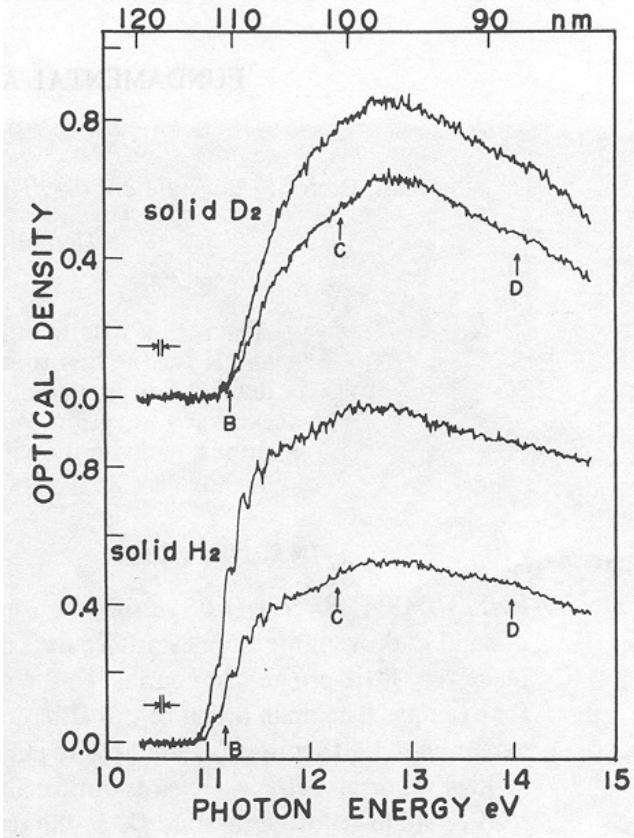


[Hemley et al. (1996);
see also Chen et al. (1996)]

Optical/Infrared Absorption of Hydrogen at Very High Pressures



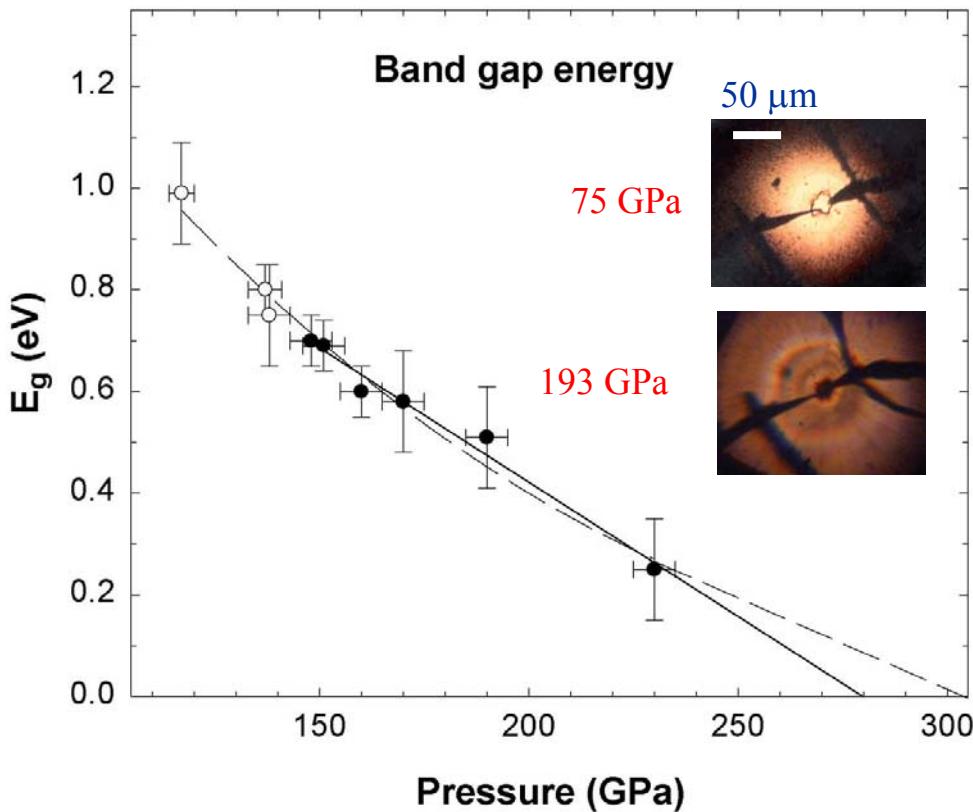
Absorption Edge (zero pressure)



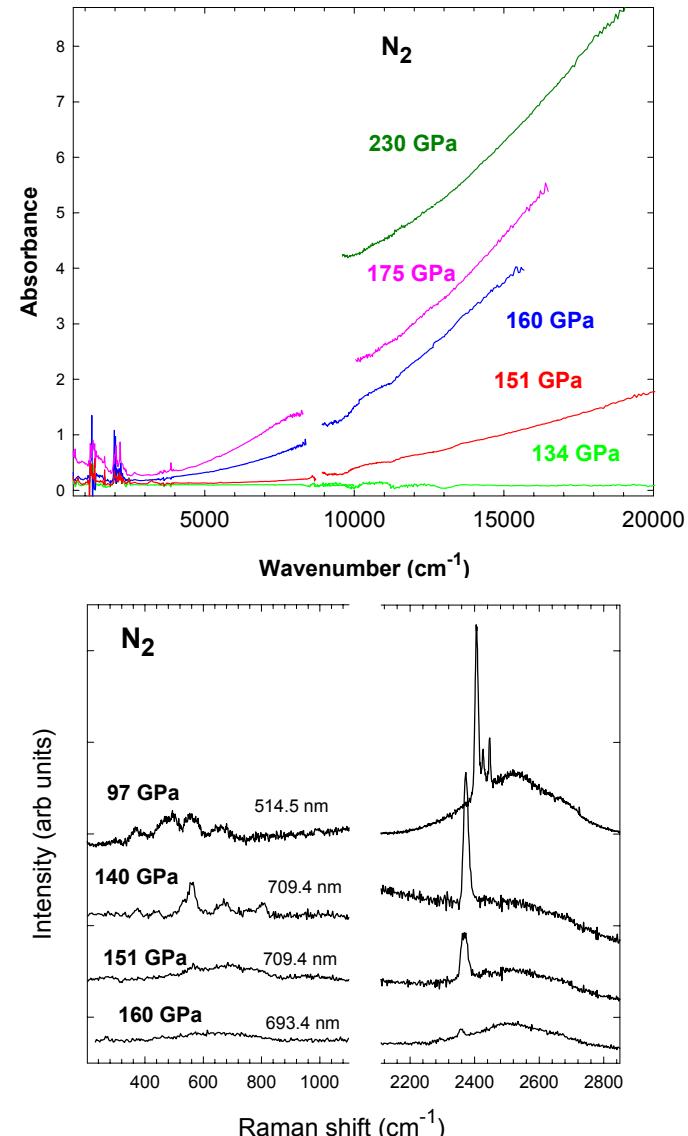
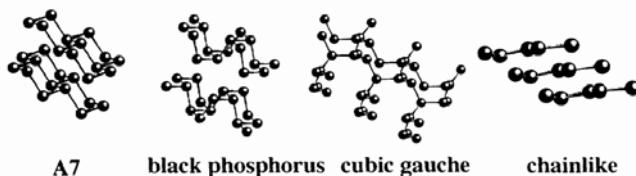
➤ Pressure dependence from IXS

Pressure Induced Dissociation of Nitrogen: SYNCHROTRON INFRARED ABSORPTION

[Goncharov *et al.*, *Phys. Rev. Lett.* 82, 1262 (2000) Eremets *et al.*, *Nature* 411, 170 (2001)]



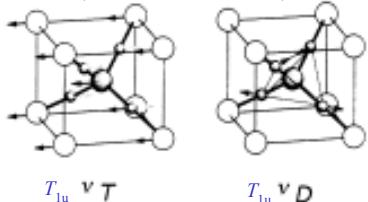
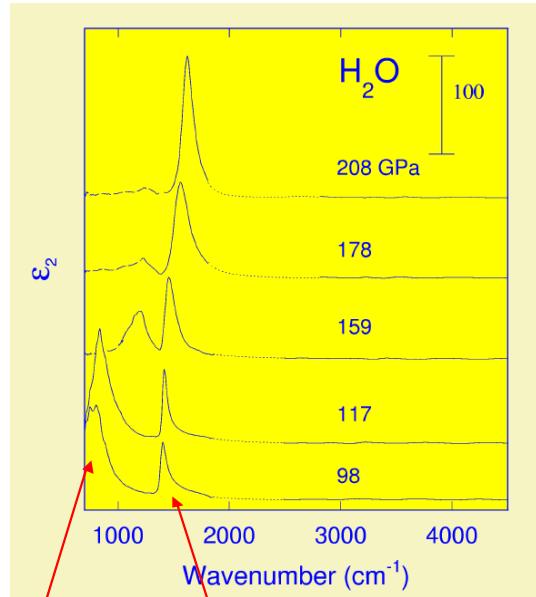
- Semiconducting to 230 GPa
- Consistent with electrical conductivity
- Loss of vibron – polymeric phase



H₂O TO MEGABAR PRESSURES: Combination of IR and X-ray Diffraction

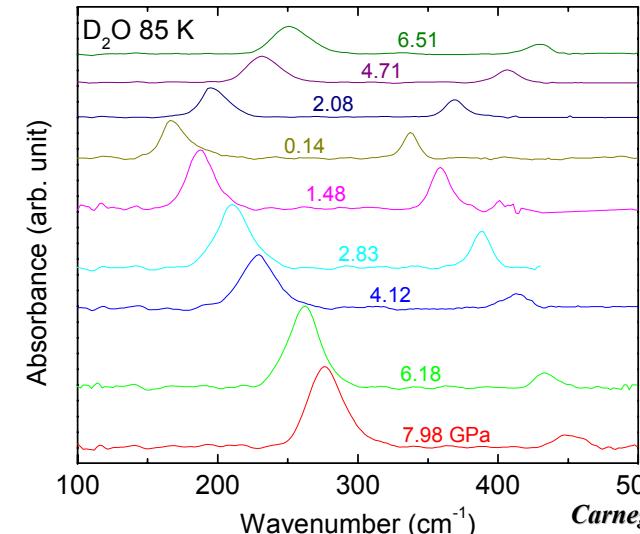
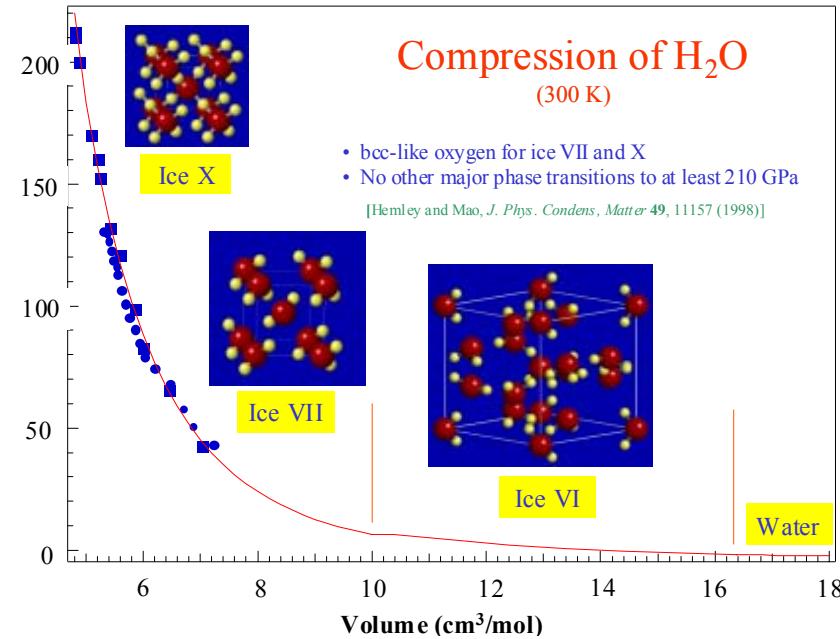


HIGH PRESSURE SPECTRA Synchrotron Infrared Reflectivity



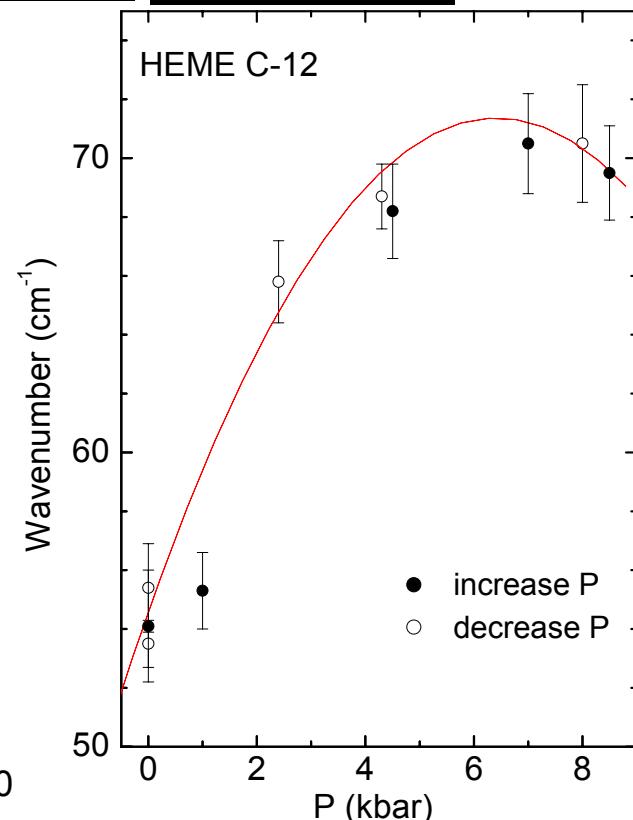
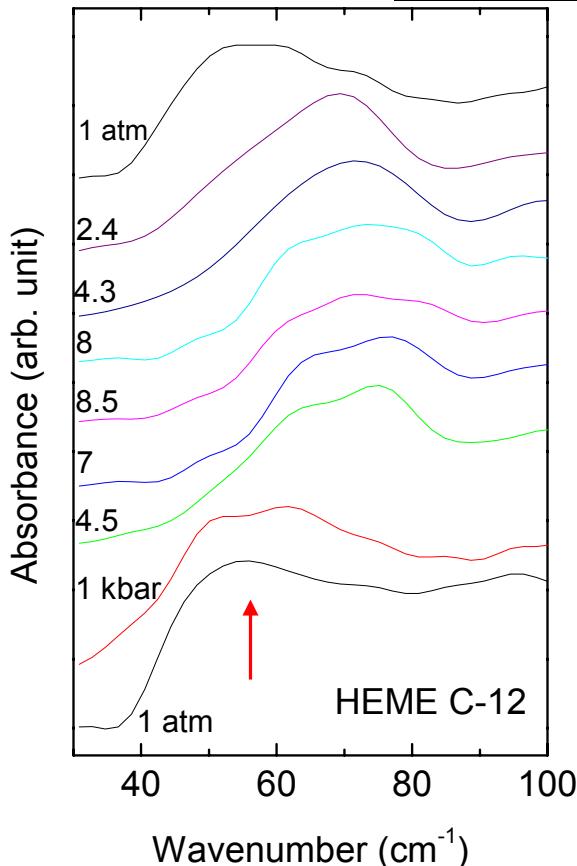
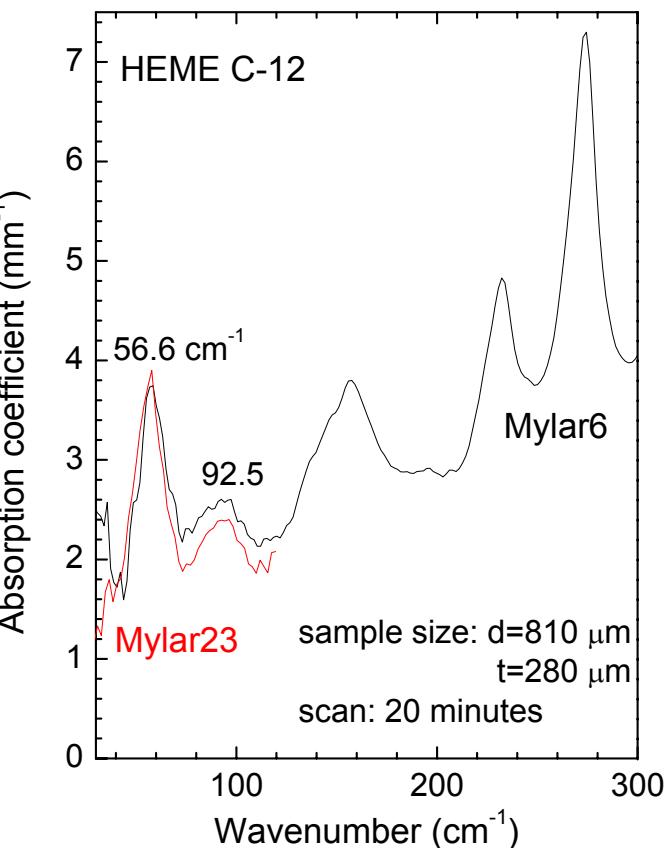
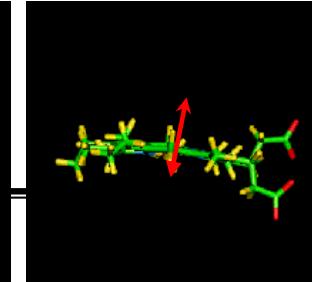
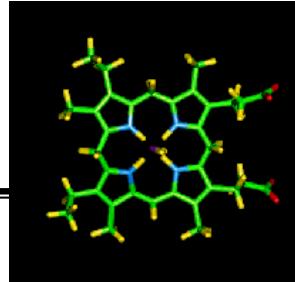
[Goncharov *et al., Science*
273, 218 (1996)]

- Non-molecular ice first identified by IR reflectivity above 60 GPa
- X-ray confirms bcc-based structure
- New far-IR absorption



Carnegie Institution

Organic Systems: HEME DOMING-MODE



- Doming mode found at 57 cm^{-1}
- Large pressure shift (consistent with assignment)
- Far-IR at high pressure (large anvils)

[Klug et al., Proc. Nat.
Acad. Sci. 99, 12526 (2002)]

NEXT GENERATION HIGH-PRESSURE DEVICES: Hybrid High-Pressure/CVD Anvils

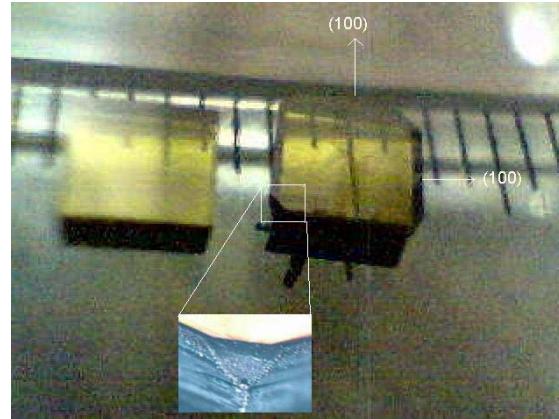


Size Limitations of Conventional Devices

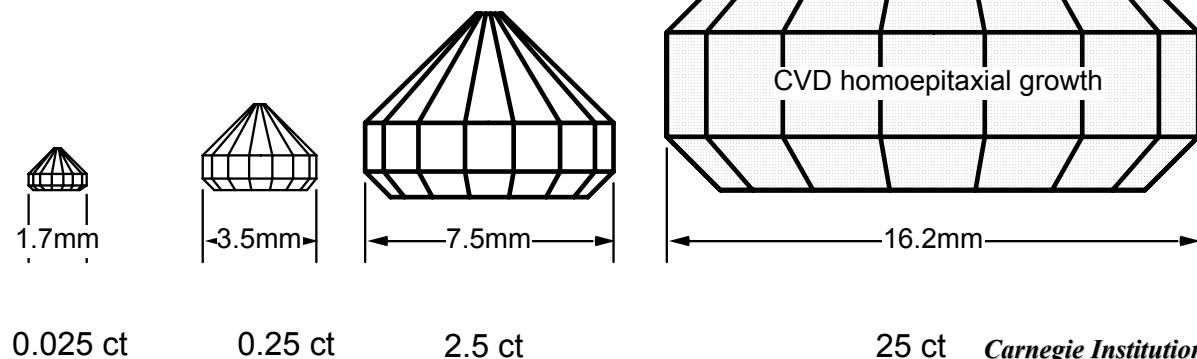
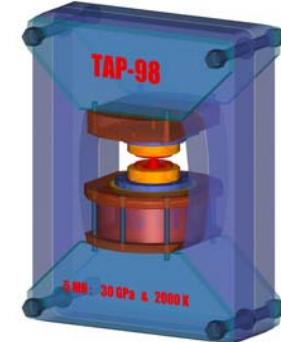
- Sample bridging in the small sample chamber
- Heat damage of the anvil due to thin samples\
- Temperature accuracy/precision compromised
- Applications of several simultaneous probes limited



Growth of Diamond Anvils by Homoepitaxial Chemical Vapor Deposition: **"Large Volume" Diamond Cell**



[Yan et al. PNAS 99, 12523 (2002)]



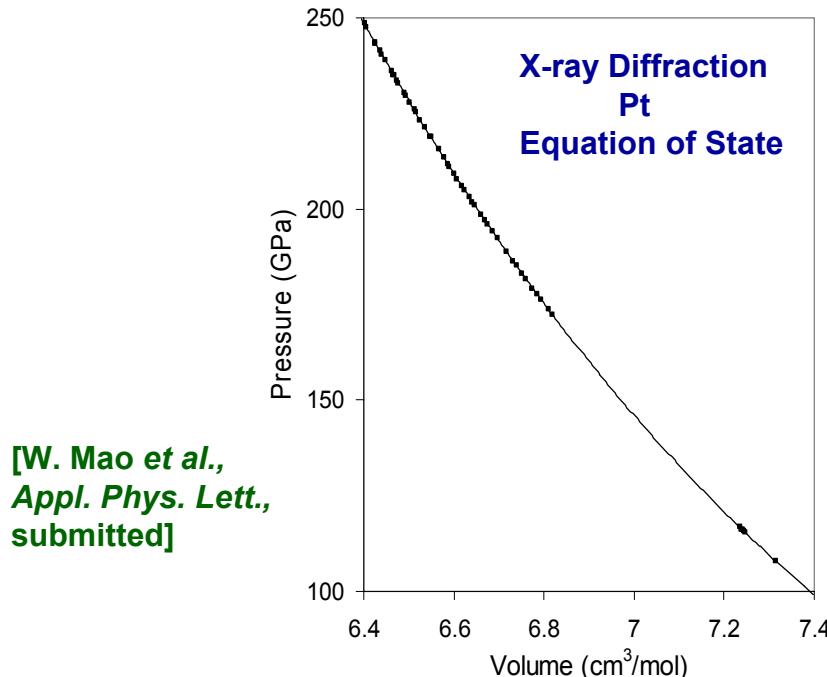
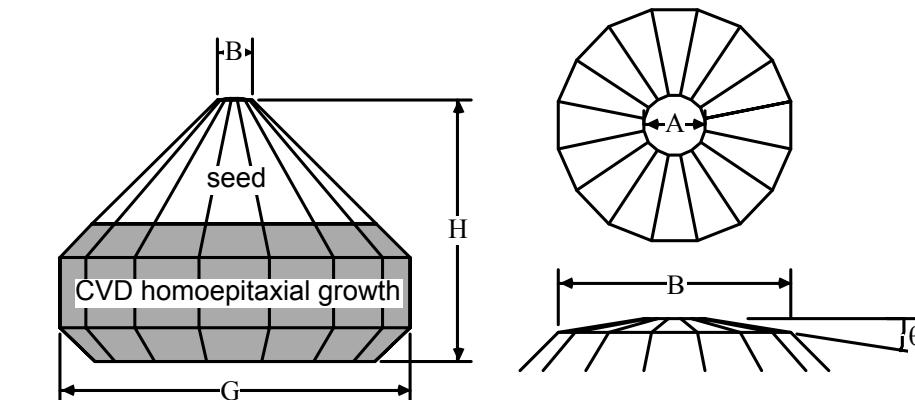
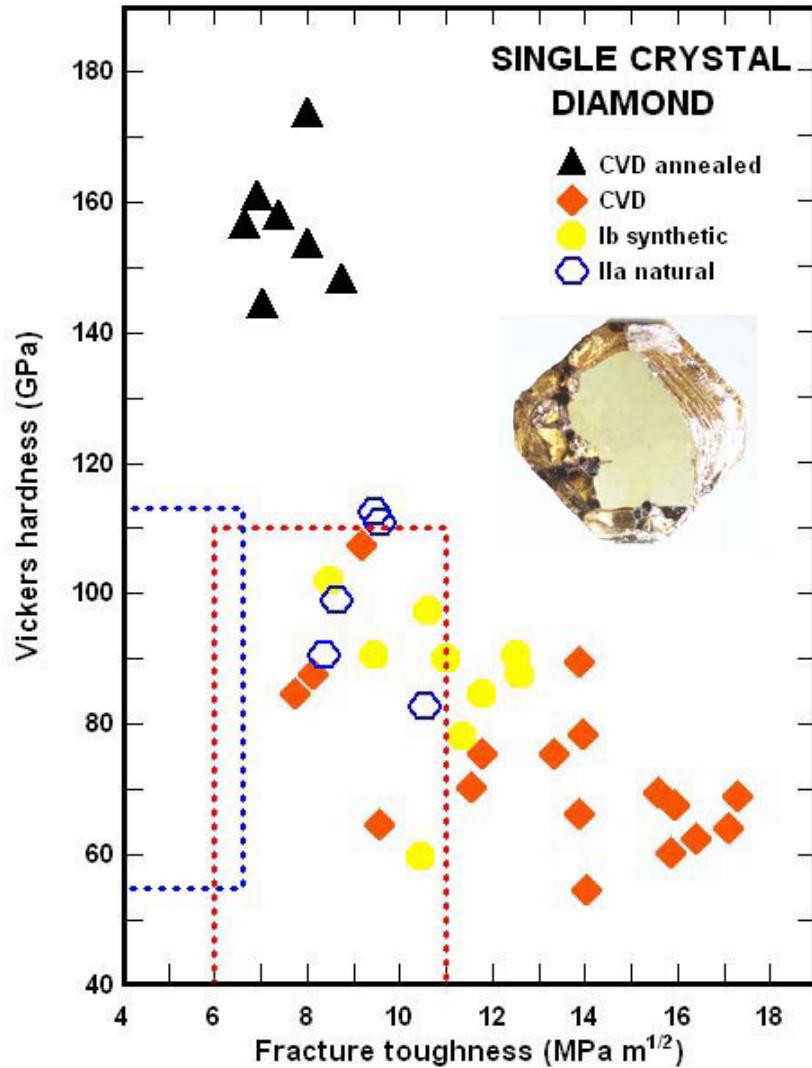
0.025 ct

0.25 ct

2.5 ct

25 ct Carnegie Institution

LARGE VOLUME MEGABAR CELLS: CVD Single Crystals are Ultrahard and Generate >200 GPa Pressures



[W. Mao et al.,
Appl. Phys. Lett.,
submitted]

- Annealing at 2000 K and 7 GPa
- Vickers hardness ~ 160 GPa [Yan et al., *Nature*, submitted]

GENERAL CONCLUSIONS



1. New high-pressure/synchrotron radiation techniques provide important new tools for studying strongly correlated electron systems
2. Bright microbeams from the hard x-ray (diffraction, inelastic scattering) and in the near- to far-IR (absorption, reflectivity) range are essential.
3. These need to be integrated with other probes/techniques (ultralow T, magnetic fields, transport, laser methods)
4. New high-pressure methods (e.g., CVD single-crystal diamond techniques) will allow a new generation of high-pressure experiments.
5. All are needed for understanding myriad phenomena being uncovered in new high pressure experiments

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